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Catalytic Oxidation of Olefinic Hydrocarbons

W. L. FAITH and M. S. DENDURENT

Kansas State College, Manhattan, Kansas

AMYLENE may be converted to maleic acid by vapor-phase oxidation over a V_2O_5 catalyst. At temperatures between 350 and 500°C., from 12 to 22 percent conversions to maleic acid are obtained. The optimum temperature is about 425°C. Variations in space velocity and air-amylene ratio have little effect on percentage conversion.

Hexene, heptene, and octene also yield maleic acid by the same process. Conversions are higher than those from amylene, and appear to increase as the number of carbon atoms in the hyrocarbon is increased.

A discussion of economic possibilities of the process is included.

IN the past several years great interest has been shown in the chemical utilization of petroleum hydrocarbons. The greatest interest has centered around olefinic hydrocarbons because of their higher reactivity. From the standpoint of the production of chemicals only, the chief processes which have been reported are: chlorination with subsequent hydrolysis, nitration, esterification, and hydration. Oxidation reactions have not been particularly successful. Direct air oxidation has failed because of difficulties involved in controlling the reaction so as to produce intermediate oxidation products. On the other hand, the use of chemical oxidizing agents involves the added expense of the oxidizing agent and intricate purification processes.

Work in this laboratory on the oxidation of organic compounds containing double bonds[3, 4] indicated that the catalytic vapor-phase oxidation of olefins might produce good yields of maleic acid. In 1931, Shimose[10] reported that certain olefins yielded maleic acid upon air oxidation over vanadium pentoxide catalyst, but did not list the yields obtained. Subsequently, a patent assigned to Carbide and Carbon Chemicals Corporation[11] claimed a 20 percent conversion to maleic acid by the vapor-phase oxidation of butenes over vanadium pentoxide and related catalysts.

The purpose of the present work was to study satisfactory conditions for the oxidation of higher olefins to maleic acid.

APPARATUS

The apparatus used in this study was of the usual type employed in the laboratory for catalytic vapor-phase oxidations. The olefin to be oxidized was vaporized by bubbling nitrogen through the liquid hydrocarbon. Nitrogen was used instead of air so as to reduce the explosion hazard in the vaporizer. In order to fix the vapor pressure of the olefin it was held at a constant temperature. The olefin-nitrogen gaseous mixture was then mixed further with a large excess of dry air (measured by means of a U-tube flowmeter) just prior to entering the catalyst chamber. The catalyst chamber was a pyrex tube 2.5 centimeters in diameter and 36 centimeters long. Catalyst lengths were varied from 8 to 36 centimeters. Heat was supplied to the catalyst chamber by a combustion furnace which surrounded it. Temperature measurement was by means of a movable thermocouple inside a small pyrex tube projecting into the center of the catalyst. In all cases the temperature of the catalyst was taken at the hottest point in the chamber. The reaction gases were led from the catalyst chamber into a large flask cooled externally by an ice-water mixture. Solid maleic acid (or anhydride) sublimed on the walls of this flask. Any unsublimed acid was then scrubbed from the gases in a series of gas washing bottles partially filled with water.

The vanadium oxide catalyst was prepared by precipitation on aluminum turnings by the action of oxalic acid on ammonium metavanadate. The adhering ammonium oxalate was removed by heating in a current of air. One such catalyst was used for over 250 hours without apparent reduction in activity.

METHODS OF ANALYSIS

At the end of each run, the contents of the flasks in the washing train were combined and made up to volume for analysis. Total acidity was determined by titration and aldehydes were determined by the neutral sodium sulfite method.[6] Maleic acid was determined by the barium maleate monohydrate method of Milas and Walsh[7] as modified by Faith and Schaible.[8] The maleic acid obtained from each different olefin was identified by melting point and by conversion to fumaric acid by the action of light in the presence of bromine.

Carbon dioxide was determined by passing a portion of the reaction gases in each run through a flowmeter and thence into a barium hydroxide solution. The resulting barium carbonate precipitate was dissolved in dilute hydrochloric acid and determined by conversion to barium sulfate in the usual manner.

Attempts to identify aldehydes and other acids than maleic showed that mixtures were present in both cases. Qualitative tests indicated that the chief constituents were formaldehyde and formic acid respectively. Ac-

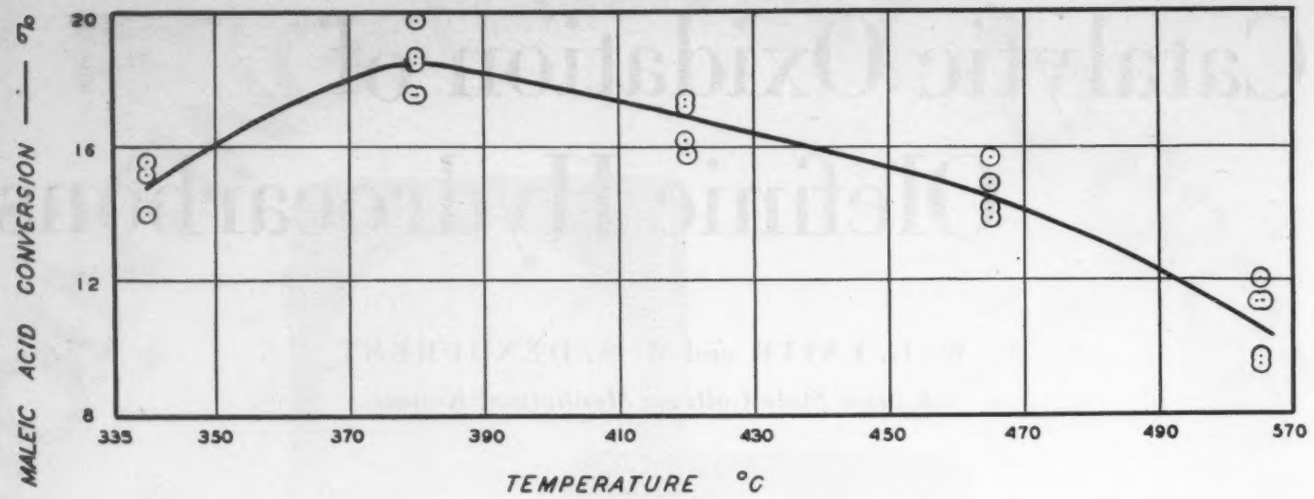

FIGURE 1

Catalytic Oxidation of Amylene.

cordingly aldehyde and "other acid" conversions were calculated in mole percent.

SCOPE OF STUDY

During the course of the study the following olefins were oxidized: Pentene-2, trimethylethylene, technical amylene, methyl pentene, heptene, and caprylene (octene).

The major portion of the data was taken on the oxidation of technical amylene (Eastman Kodak Company). Consequently, complete figures on the effect of the chief variables (temperature, air-hydrocarbon ratio, and space velocity) are not available on all the hydrocarbons mentioned. A sufficient number of runs were made, however, on the other hydrocarbons mentioned to show that they followed essentially the same pattern as the amylene.

OXIDATION OF FIVE-CARBON OLEFINS

Effect of temperature—The independent effect of temperature on the reaction is shown in Tables 1, 2, and 3 for pentene-2, trimethylene, and technical amylene respectively. A graph of the figures in Table 3 is shown in Figure 1. It will be noticed that all points do not fall on a smooth curve. This is not the result of faulty analysis, but because of the impossibility of accurate temperature control in the catalyst chamber. In a laboratory apparatus of this type a considerable temperature gradient exists from the entrance to the chamber to the point of maximum temperature. The recorded temperature, as mentioned above, was always that at the maximum point. Furthermore this maximum point shifted from one run to another with a change in the other variables. For that reason these other variables were maintained as constant as possible in runs considered here.

In general the figures show that maximum conversions are obtained between 375 and 450°C. (707-842°F.)

No generalities can be made concerning total oxidation (i.e. conversion to CO_2) as great variations were noticeable. This is probably due to failure to obtain a representative sample of the exhaust gases. A slight fluctuation in catalyst temperature during the time of the carbon dioxide determination could result in completely erroneous carbon dioxide conversions.

It will be noticed, however, that "other acid" formation shows a definite tendency to decrease as the temperature is increased. It may be that more accurate figures on carbon dioxide conversions would show that at the higher temperatures these "other acids" were completely oxidized to carbon dioxide. On the other hand, aldehyde formation does not appear to be linked with carbon dioxide conversions, but seems to reach a maximum at about the same temperature as does maleic acid.

From a practical standpoint it can be said that oxidation at any temperature between 350 and 500°C. (662-932°F.) would result in maleic acid conversions around 17± 5 percent. At the high temperatures there would be less danger of contamination from aldehydes and "other acids."

Effect of space velocity—Space velocity was varied from about 2 reciprocal hours up to about 40 reciprocal hours (volume of hydrocarbon gases at standard conditions per unit volume of catalyst per hour). A study

TABLE 1

Catalytic Vapor Phase Oxidation of Pentene—2

Run No.	Air-hydrocarbon ratio	Temp. (°C)	Space Velocity (recip. hours)	CONVERSIONS			
				Maleic Acid Percent	Excess CO_2* Percent	Other Acid† Percent	Aldehyde‡ Percent
33	177	260	22.20	0.0	0.1	2.6	3.3
32	171	340	22.70	6.7	1.8	6.6	8.4
28	181	380	21.65	16.6	11.6	9.1	16.8
21	184	420	21.15	18.4	14.6	8.7	19.8
87	179	465	21.65	15.0	12.7	1.6	19.6
88	198	505	19.60	11.0	16.7	1.0	17.9

* Based on complete oxidation to CO_2; does not include CO_2 accompanying maleic acid formation.
† Calculated as mole percent monobasic acid.
‡ Calculated as mole percent.

TABLE 2

Catalytic Vapor Phase Oxidation of Trimethylethylene

Run No.	Air-hydrocarbon ratio	Temp. (°C)	Space Velocity (recip. hours)	CONVERSIONS			
				Maleic Acid Percent	Excess CO_2* Percent	Other Acid† Percent	Aldehyde‡ Percent
60	223	260	16.80	0.0	0.9	7.5	40.0
59	242	340	15.47	13.4	5.3	9.1	12.3
58	240	380	15.62	14.8	7.4	8.4	16.7
55	247	420	15.47	18.0	13.0	6.9	23.2
53	234	465	15.98	18.5	16.8	4.9	....
61	268	505	13.92	9.4	20.5	0.7	17.3

* Based on complete oxidation to CO_2; does not include CO_2 accompanying maleic acid formation.
† Calculated as mole percent monobasic acid.
‡ Calculated as mole percent.

TABLE 3

Catalytic Vapor Phase Oxidation of Technical Amylene (Eastman) Effect of Temperature

Run No.	Air-hydrocarbon ratio	Temp. (°C)	Space Velocity (recip. hours)	CONVERSIONS			
				Maleic Acid Percent	Excess CO_2* Percent	Other Acid† Percent	Aldehyde‡ Percent
177	660	340	2.66	15.3	11.0	10.1	9.9
146	440	340	3.96	15.6	11.6	10.9	8.9
193	505	340	5.18	14.1	1.9	11.1	7.4
143	430	380	4.05	18.7	16.6	3.7	11.8
191	480	380	5.45	19.8	10.0	7.1	14.3
213	465	380	5.20	17.6	16.5	4.8	16.2
189	395	380	6.76	17.6	3.9	8.4	11.5
222	390	380	6.84	18.6	4.5	8.2	11.2
160	470	420	3.78	17.4	25.5	3.0	9.6
156	475	420	3.67	16.2	20.5	1.4	10.5
164	490	420	3.65	15.8	14.1	0.6	11.3
150	390	420	4.53	17.2	23.7	2.4	10.7
218	465	465	5.21	14.9	6.6	1.4	14.3
169	545	465	3.33	13.8	1.1	0.3	9.4
154	515	465	3.50	15.7	22.1	0.0	9.0
142	350	465	4.90	14.1	15.2	0.4	6.2
145	470	505	3.75	11.4	22.8	0.1	5.0
182	450	505	3.77	12.0	21.1	0.5	8.4
181	430	505	3.92	9.7	8.8	0.8	8.1
155	485	505	3.60	9.6	23.2	2.8	4.2
184	570	505	2.95	11.4	14.8	0.8	9.7

* Based on complete oxidation to CO_2; does not include CO_2 accompanying maleic acid formation.
† Calculated as mole percent monobasic acid.
‡ Calculated as mole percent.

in maleic acid conversions. If any difference is apparent, it is a slight increase in conversion as the ratio is increased.

OXIDATION OF HEXENE, HEPTENE, AND OCTENE

The hexene used in this study was Eastman's methyl pentene; the heptene was obtained from Carbide and Carbon Chemicals Corporation, and the octene was Eastman's caprylene (probably a 50-50 mixture of octene-1 and octene-2).

The results obtained by oxidizing these hydrocarbons are shown in Table 5. In the limited number of runs made the effect of the several variables seemed to be about the same as those with amylene. The greatest noticeable difference in the results is the increased conversion to maleic acid as the number of carbon atoms in the molecule is increased. In ascending from 5 to 8 carbons, the approximate relative conversions to maleic acid are 19, 25, 27, and 30 percent respectively.

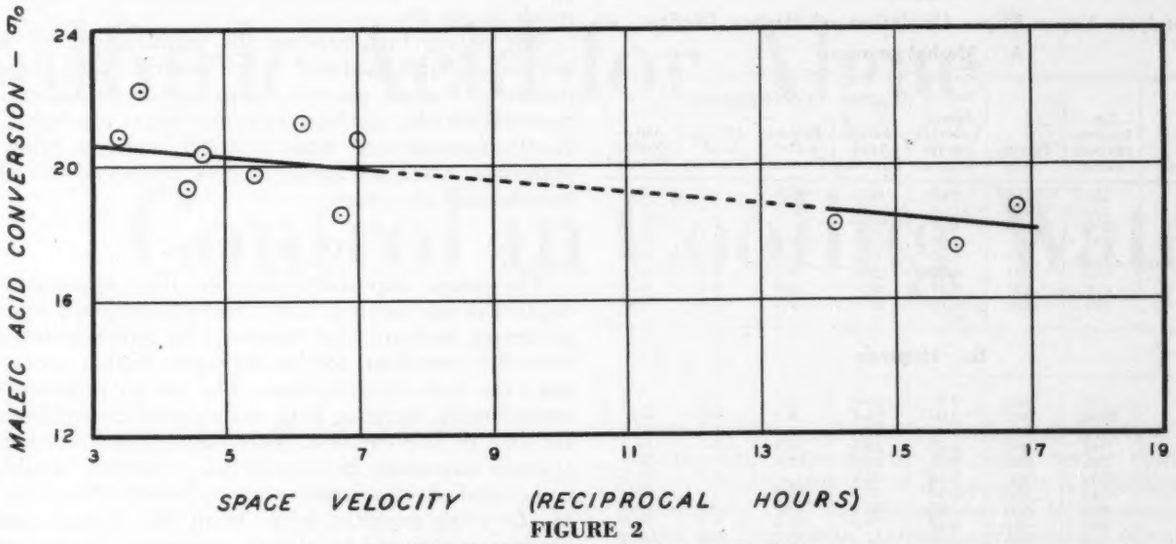

FIGURE 2

Catalytic Oxidation of Amylene at 380° C.

of the tables shows that there is not a great deal of variation in the maleic acid conversion attributable to changes in space velocity. Table 4 and Figure 2 show the effect of space velocity on conversions of amylene to maleic acid at 380°C. The deviation of the points from the curve in Figure 2 is again probably due to temperature variations.

Effect of air-hydrocarbon ratio—The ratio of air to hydrocarbon is limited by practical considerations to those mixtures within the non-explosive range (less than 1.6 percent amylene). This corresponds to air-amylene ratios above 61.5. Although this is roughly equivalent to 100 percent excess air, an even greater excess is desirable in order to remove excess heat from the reaction zone. However, air-hydrocarbon ratios above 100 make little difference in maleic acid conversions. A plot of air-amylene ratio against maleic acid conversion at 380°C. is shown in Figure 3. Insufficient runs were available to plot only those at the same space velocity. This probably accounts somewhat for the scattered points. The graph does show, however, that varying the air-amylene ratio makes very little difference

IMPORTANCE OF MALEIC ACID

The manufacture of maleic acid from olefinic hydrocarbons is a process of potentially great economic possibilities. At present maleic acid is made from benzene

TABLE 4

Catalytic Vapor Phase Oxidation of Technical Amylene (Eastman) Effect of Space Velocity

Run No.	Air-hydrocarbon ratio	Temp. (°C)	Space Velocity (recip. hours)	CONVERSIONS			
				Maleic Acid Percent	Excess CO_2* Percent	Other Acid† Percent	Aldehyde‡ Percent
153	525	380	3.41	20.9	18.2	1.8	15.5
196	710	380	3.76	22.3	17.8	8.7	19.3
216	540	380	4.46	19.4	5.0	8.4	18.3
190	570	380	4.64	20.4	4.8	14.9	15.2
191	480	380	5.45	19.8	10.0	7.1	14.3
220	410	380	6.15	21.3	11.2	6.5	20.7
222	390	380	6.84	18.6	4.5	8.2	11.2
135	240	380	7.00	20.8	14.0	4.9	12.1
223	195	380	14.10	18.3	7.0	6.7	14.4
127	250	380	15.90	17.6	12.9	6.1	11.2
199	475	380	16.80	18.8	5.6	5.9	10.8

* Based on complete oxidation to CO_2; does not include CO_2 accompanying maleic acid formation.
† Calculated as mole percent monobasic acid.
‡ Calculated as mole percent.

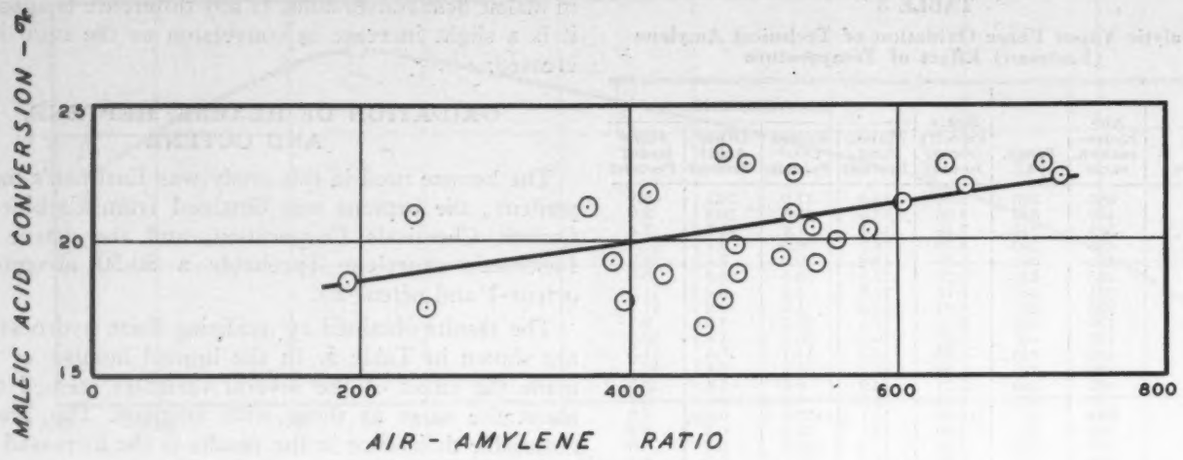

FIGURE 3

Catalytic Oxidation of Amylene at 380° C.

TABLE 5

Catalytic Vapor Phase Oxidation of Higher Olefins

A. Methyl pentene

Run No.	Air-hydrocarbon ratio	Temp. (°C)	Space Velocity (recip. hours)	CONVERSIONS: Maleic Acid Percent	Excess CO_2* Percent	Other Acid† Percent	Aldehyde‡ Percent
230	480	340	8.95	10.0	6.5	8.0	5.2
229	390	340	11.20	4.5	1.2	3.3	3.2
224	2700	380	1.37	23.3	....	7.2	18.6
225	1300	380	3.02	24.5	7.6	9.1	17.3
228	895	380	4.80	23.9	7.6	8.8	14.8
227	950	420	4.42	22.6	8.7	5.3	14.4
226	470	420	8.87	26.7	12.0	6.1	19.4
231	375	420	11.10	27.9	2.3	3.9	20.9

B. Heptene

236	750	340	5.48	10.5	3.5	7.0	7.8
234	2060	380	2.02	24.7	8.4	5.3	20.5
233	1370	380	3.35	23.3	8.4	6.7	15.8
235	940	380	4.43	25.4	10.4	5.5	19.5
239	700	380	6.27	24.4	18.0	6.2	15.9
232	3800	380	1.10	20.8	....	0.0	12.2
238	1340	420	2.90	27.2	17.5	3.3	23.4
237	680	420	5.90	26.1	19.4	3.8	18.4
241	960	465	4.48	23.8	20.5	6.0	20.8
240	715	465	5.70	27.0	33.7	1.8	20.5
242	550	505	7.58	25.9	23.0	1.2	18.6

C. Octene

249	485	340	8.52	18.3	3.6	8.4	22.9
246	2400	380	1.78	31.0	7.4	2.5	30.0
247	1980	380	2.30	32.3	26.0	6.7	23.1
245	1790	420	2.48	32.7	23.0	2.6	32.7
244	1310	420	3.28	31.3	16.0	3.2	23.6
248	430	420	9.60	25.0	16.3	5.1	22.2
251	455	465	9.10	30.0	23.7	3.0	31.8
250	445	505	9.30	30.6	24.5	0.4	28.2

* Based on complete oxidation to CO_2; does not include CO_2 accompanying maleic acid formation.

† Calculated as mole percent monobasic acid.

‡ Calculated as mole percent.

by a similar process to the one described above. However, benzene is considerably more expensive than the lower olefinic hydrocarbons. With the probability that further work will raise the percentage conversion of olefins to maleic acid, the process should be able to compete favorably.

Also there is little doubt that maleic acid will become more important in the future than it is at present. Besides its use in manufacturing such derivatives as succinnic and malic acids, several companies are now using it in the manufacture of plastics and plasticizers. In all probability lower manufacturing costs will result in much larger use.

The patent literature on the manufacture of maleic acid is evidence in itself of the interest being shown by industry. Recent patents claim its manufacture from crotonaldehyde,[2] cyclopentadiene,[1] butyl alcohols,[11] furfural[8], naphthenes,[9] and diphenyl,[5] among other raw materials. Over all these, olefinic hydrocarbons should have a cost advantage.

FUTURE WORK

The most important variable that remains to be studied is the catalyst itself. Results on other oxidation processes indicate that mixtures of molybdenum oxide with the vanadium oxides may give higher yields than the vanadium catalyst alone. The use of promotors will undoubtedly increase both maleic acid conversions and the life of the catalyst. This last factor, which is extremely important in commercial processes, would have to be studied in a larger scale apparatus than was used in the work reported here. With this larger scale apparatus one would be able to maintain a more constant temperature in the catalyst chamber by employing various methods of temperature control. Such control is vital in securing maximum conversions.

Acknowledgment is herewith made to Carbide and Carbon Chemicals Corporation who furnished the methyl pentene and heptene; to Sharples Solvents Corporation for part of the pentene-2; to Vanadium Corporation of America for ammonium metavanadate; to R. R. Freeman who made some of the runs on penetene-2 and trimethylethylene.

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Sulfuric Acid for Algae Control in Cooling Water

RUSSELL D. KOONS

CONTROL of microscopic organisms classed under the general term of algae is of importance to industries that utilize water as a cooling agent. Heat transfer losses and poor temperature control have been shown in the past to have been caused by this type of plant growth.

Various methods for the control and elimination of algae growths have been suggested; some of these are as follows:[1]

a. Copper sulfate.
b. Chlorinated by either free chlorine or by calcium hypochlorite.
c. Use of a coagulent followed by lime.
d. Sulfuric acid.
e. Organic specifics.

Choice of a method depends upon the type and size of cooling-water system, type of water, type of algae, cost, and ease of operation and control.

At the Norwalk refinery of Wilshire Oil Company, 15 miles southeast of Los Angeles, the range of mean temperatures is 60-80°F. In this refinery considerable difficulty was encountered because of algae growth in the cooling-water system.

For the treatment of cracked distillates the plant uses a cold-sulfuric-acid process followed by two water washes. The disposal of this wash water containing sulfuric and sulfurous acids presents a problem. Approximately 1400 barrels per day of this water, added to the cooling-water system, accomplished the desired objective, algae control, but as the concentration of the acid-water increased in the system, foaming troubles developed. But it is possible that with other equipment this type treatment would have been successful. Because of the foaming troubles, the use of acid-water was discontinued and commercial 98 percent sulfuric acid was used in its place. The following information is based upon the use of this acid in cooling water conditioning.

COOLING SYSTEM

The refinery cooling-water system contains approximately 613,000 gallons. This water is contained by an 800-foot tower, under which is a 400,000-gallon cement reservoir, closed condensers, and 3 open box condensers. The reservoir under the tower is from 2 to 14 feet deep and drains into a weir at the deep end. Pumps force the water through the closed system condensers and over the top of the tower. These pumps also supply water to the open-box condensers. Water from the open condensers gravitates to a well where it is picked up and pumped over another section of the tower. The circulation rate is approximately 50 minutes per cycle. The make-up water for this system comes from a 100,000-barrel open cement-lined pond. The amount of

Table I

	ppm
Mimeral Residue @ 180° C	506
Silica (SiO_2)	12
Iron and Aluminum Oxide (R_2O_3)	33
Calcium (Ca)	15
Magnesium (Mg)	4
Bicarbonate (HCO_3)	324
Carbonate (CO_3)	9
Chloride (Cl)	70
Sulfate (SO_4)	80
Soap Hardness as $CaCO_3$	107
pH	8.5

make-up is automatically controlled by a float in the reservoir under the tower. Chemical analysis of the make-up water is given in Table 1.

Temperature of the cooling water varies between 115-125°F. at the top of the tower, and 70-80°F. at the bottom; the temperature of the water in the open condensers varies between 130-150°F. The temperature of the water in the closed system condensers does not exceed 200°F.

Before the use of acid, this system was periodically "blown-down" until the soap hardness of the water, as calcium carbonate, was less than 350 parts per million. This "blow-down," exclusive of other mechanical losses, represented approximately 25 percent of the capacity of the system.

NO CORROSION

The algae growth was centered on the top decks of the tower where the temperature of the water was high and where the organisms were exposed to sunlight. Growth occurred at other points in the system but the top of the cooling tower was the chief source of trouble.

Commercial 98 percent sulfuric acid was added to the reservoir under the tower at the shallow end by means of copper tubes acting as siphons from 12-gallon glass carboys. One to three carboys were permitted to siphon into the system during each 8-hour shift. This means of handling the acid is not permanent. An acid proportioning pump controlled automatically by pH is being considered. By adding the acid at the shallow end of the reservoir it must travel the 800 feet in the cement reservoir before coming into contact with metal, consequently there is no danger of corrosion.

The optimum pH is considered to be 7.9 — 8.1; below this value no normal carbonates exist. W. C. Purdy,[1] Plankton expert of the U. S. Public Health Service, states that by removing carbonates and bicarbonates, the source of algae food, beneficial results were obtained. Wm. C. Emigh[2] notes that the algae growth is a function of the pH of the water. He further states that water containing algae had a pH of 9.0. This value was the same as was noted at the Wilshire refinery before using sulfuric acid.

Daily samples of the cooling water were collected from three points in the system; the pH of these samples was determined by means of a saturated calomel cell and a glass electrode. Another method of control which could be used by industries not possessing a potentiometer, is to add acid until the water gives off a faint pink color with phenolphthalein indicator; this represents a pH value of 8.0 — 8.2. However, where possible, a more precise method is recommended. From the daily pH values the amount of acid to be added was estimated. The amount necessary varied from 800 to 1500 pounds per day, depending upon the quantity of water circulated, the "blow-down," and amount drawn off for other plant purposes.

OPERATING RESULTS

While acid treatment was being used, the "blow-down" was decreased and so adjusted as to keep the total solids under a pre-determined arbitrary limit. In order to keep the total solids under 4000 parts per million the "blow-down" was approximately 8 percent per day. The total solids were determined daily by a hydrometer as is commonly used for boiler-water concentrations; these values obtained by the hydrometer were checked weekly by evaporation and were found to be in close agreement. Table 2 gives the concentration encountered after treatment and circulation at the end of three different refinery runs.

The total solids were progressively increased by decreasing the amount of "blow-down;" this was done to decrease both pumping and treating costs. Recent runs at higher concentrations have demonstrated that 4000 parts per million total solids may be exceeded without accompanying difficulties.

OTHER BENEFITS

During each shutdown of the refinery the closed system condensers were opened and inspected for slime growth, scale deposits and corrosion. The condensers showed none of the above objectionable features. It may be stated here that the primary purpose of sulfuric acid treatment of cooling water was for algae control, but there is also a secondary benefit. If the pH of the water is maintained under 8.0, normal carbonates do not exist, hence no precipitation of calcium or magnesium carbonates as scale. The normal carbonate is replaced by sulfate. No deposit of calcium sulfate was noted by concentrations of total solids up to 4000 parts per million. Betz[3] in an article entitled *Corrosion of Cooling Water* gives a discussion of sulfuric acid as a preventive for scale formation.

At first glance the cost of the acid required appears to be excessive, but during the refinery runs mentioned above the savings in maintenance costs on condensers alone was 1.8 times as great as the cost of the acid used. Besides this saving, there are other benefits, increased heat transfer, reduced pumping costs, and intangible savings.

In general the results obtained by the use of sulfuric acid for algae control have been satisfactory. Growth on the tower was retarded; no appreciable slime accumulated in the condensers, scale or corrosion troubles were not encountered.

It should be emphasized that this type of water treatment requires close supervision.

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Table II

Length of Run, Days:	33 Days	29 Days	66 Days
Mineral Residue @ 180° C	3020	3870	3850
Silica (SiO_2)	53	98	406
Iron and Alun inum Oxide (R_2O_3)	47	75	48
Calcium (Ca)	156	154	194
Magnesium (Mg)	25	38	39
Bicarbonate (HCO_3)	305	250	128
Carbonate (CO_3)	72	24	0
Chloride (Cl)	344	425	376
Sulfate (SO_4)	1530	2357	2087
Volatile and Organic	114	107	143
(Soap Hardness as $CaCO_3$) (Above results in parts per million)	564	735	835
Average pH for period of the run	8.5	8.2	8.1
Average acid rate in lbs./day	850	910	980
Average total solids in ppm	....	....	3990

Experimental Studies on

Non-Fluid Lubrication

PART II-B*

High Temperature Reactions of Addition Agents. B. Chemical Surface Reactions and the Coefficient of Dry Friction.

S. KYROPOULOS

California Institute of Technology, Pasadena

IN the preceding part it was shown in experiments on cast iron or steel on steel that under conditions where non-fluid lubrication plays a considerable part, as for example in cylinder-piston ring lubrication, the effect of oiliness ingredients consists principally in chemical reactions with the overloaded peaks of the surfaces.

Thus, a steel surface, more or less cleaned by the chemical action of oil decomposition under ordinary conditions, may be made less prone to welding seizure by the formation of an oxide, nitride or other layer on the surface.

1. *General aspects and limitations of the problem.*— The present investigations scarcely need further comment with respect to the original objective of the study, viz., the gaining of fundamental information on the connection between wear and seizure in cylinders, or more generally, applying to steel-on-steel lubrication with use of addition agents. Such information would be particularly valuable in view of many contradictions and difficulties presented by the application of the orientation hypothesis.

In view of the close connection of the phenomena with polishing processes in general and, more especially, with the work of Bowden and co-workers, certain other applications call for discussion.

Bowden and Ridler[1] showed that on rubbing together different metals under conditions of imperfect lubrication the limiting temperature attainable is the melting point of the lower melting metal. Thus, applying our experience with high-temperature reactions to metal combinations other than steel-steel, we have to consider this limiting temperature and the possible individual reactions of the lubricant with the surface metals. This shows at once the prospects and the limitations on the further improvement of imperfect lubrication by use of the principle of "surface contamination." Thus, in the case of copper-lead bearings in imperfect lubrication there is always the danger of damage to the journal due to the high melting point of copper once it touches the steel journal and the possibility of diffusion, i.e., welding to the steel at that temperature. In this case addition of a high-temperature reactive compound to the oil, e.g., a nitriding agent, may be very useful. We understand at once why in this case a nitrided journal should show better running properties, whereas the same journal would scarcely show its advantages when running in babbitt or any of the other bearing metals which are favored by practice because they never damage the journal.

POLISHED METAL SURFACES

Copper-lead has been selected for an example because it demonstrates both the applicability of the work of Bowden and of the writer and because there is a trend in present engineering practice toward the use of bearing alloys with greater resistance to pounding and greater proneness to damaging the journal. It follows from the experiments of Bowden and Hughes[2] on polish and from the present investigation, that it is not so much the hardness as other physico-chemical properties of iron nitride which determine its better running properties.

With this example we turn our attention to the subject of surface polish. Once more combining the results of Bowden[2] and of the present work, the possibility presents itself of combining surface polish with surface contamination by high-temperature reactions with suitably selected polishing fluids. As a matter of fact most of our polished-metal surfaces are oxide surfaces due to polishing in the presence of air. Thus, high polish of a journal entails both greater smoothness and greater chemical surface protection. Strangely enough this comparative chemical inertness of the polish is sometimes attributed in the literature to the Beilby layer which, as a result of cold work, is more reactive than the undisturbed metal, rather than the reverse.

Because of the significance of these modifications of surfaces in various apparently remote fields, a series of photo-micrographs showing the polishing process of cast iron with various lubricants are presented and briefly discussed in the following section. Moreover, these pictures are a necessary supplement to the previous paper. The special experimental conditions of the material presented there and the use of an extreme pressure lubricant testing method might leave the impression that the whole investigation refers only to measureable extreme pressure conditions. The pictures show that such is not the case and that, to the contrary, the reactions already discussed show up under moderate conventionally measured loads.

2. *Microscopic investigations on surface reactions.*— Some 500 runs were made with the wear testing machine described in a previous paper.[3] Pieces of cast-iron piston ring with some natural polish, resulting from prolonged use in an internal combustion engine, constitute the test specimens. A run always starts with line contact against the journal. These initial stages of the formation of a

*For Part II. A. see Refiner, 18, 76, (320), No. 8, 1939.

Wear Prints

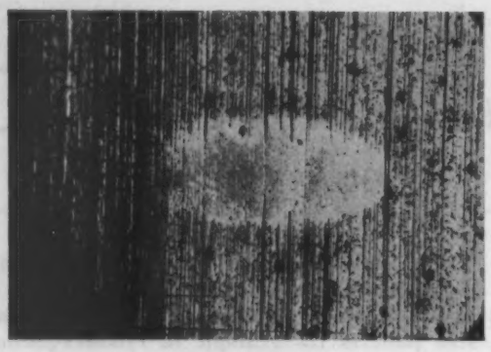

FIGURE 1 (187) 32x

FIGURE 2 (189) 126x

Light oil, Beilby and oxide layer, few crystal boundaries

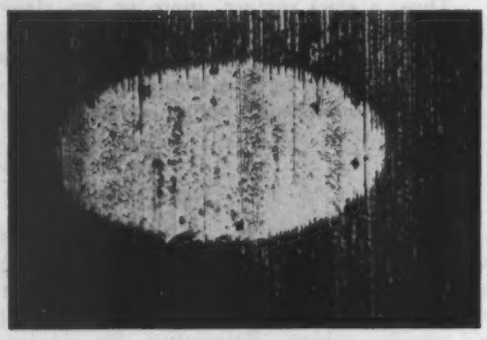

FIGURE 3 (190) 32x

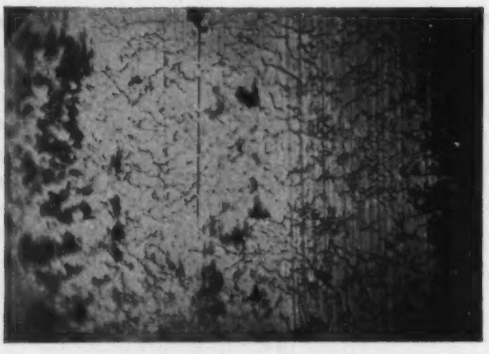

FIGURE 4 (192) 126x

Acid. Ester from paraffin wax, little oxide, many crystal boundaries

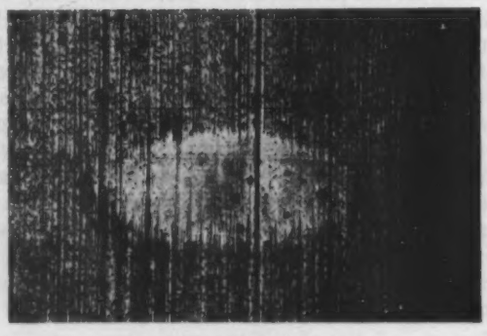

FIGURE 5 (203) 32x

Neutral n-butyl-phthalate

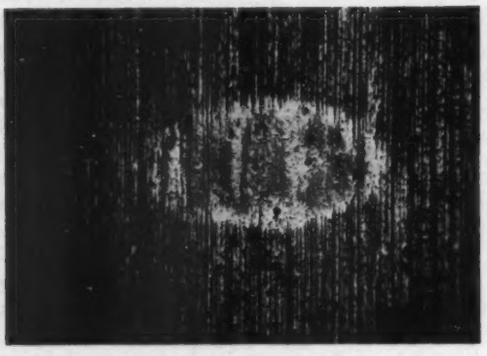

FIGURE 6 (212) 32x

Acid. Ester, high load

FIGURE 7 (213) 126x

Detail of Figure 6: both oxide and crystal boundaries

Wear Prints

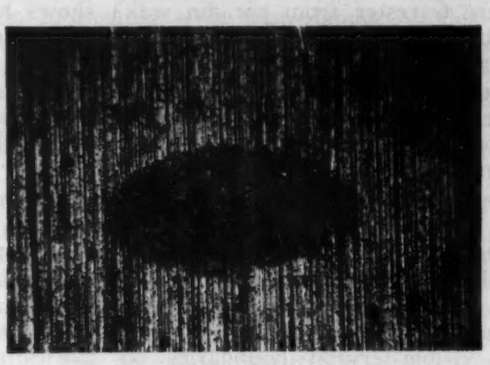

FIGURE 8 (217) 32x
Kerosene

FIGURE 9 (215) 32x
Kerosene + 2% CCl_4

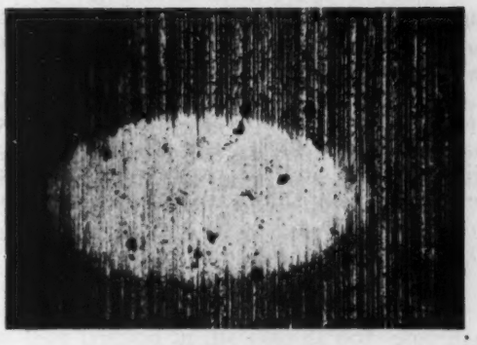

FIGURE 10 (219) 32x
CCl_4 straight

FIGURE 11 (218) 126x
Detail of Figure 8: all grainy

FIGURE 12 (216) 126x
Detail of Figure 9: grainy, crystal boundaries appear

FIGURE 13 (220) 126x
Detail of Figure 10: polish, many crystal boundaries

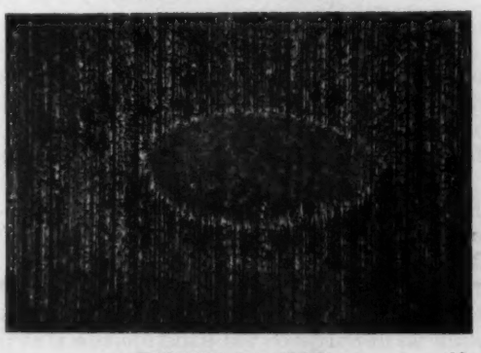

FIGURE 14 (195) 32x
Triamylamine

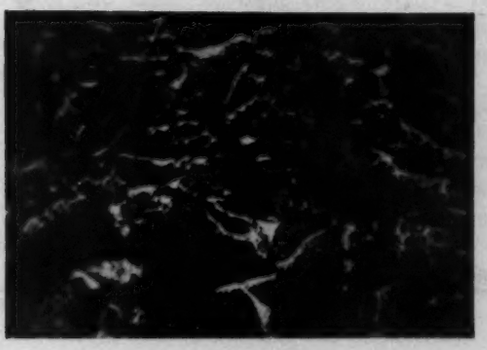

FIGURE 15 (196) 500x
Detail of Figure 14

bearing surface are not the object of our investigation. Gradually an oval wear print develops as well as a mixed type of lubrication, similar in character to the semi-fluid lubrication of practice. The load on the lever which carries the test specimen may be varied in fixed steps which were 0.5, 0.6, 0.73 and 1.85 kilograms, respectively. The loads per cm^2 are of the order of 100 kilograms. We discuss briefly a number of characteristic wear prints.

EVIDENCE FROM PICTURES

Figures 1-4—Nos. 1 and 2 are typical pictures obtained on a straight mineral oil, 2 being an enlarged section of 1; 3 and 4 are corresponding pictures obtained on straight ester from paraffin wax. The corresponding Falex seizure values are approximately 800 and 1600, respectively.[4] The oil contains no acid, the commercial ester has an acid number of about 7. We notice on the one hand, much dark haze formed within 50 minutes with mineral oil, with the boundaries of crystal grains scarcely discernible, indicating much cold work and formation of a Beilby layer[5]; on the other hand, little dark haze, very bright polish, clean crystallite boundaries on the ester specimen. The formation of the "haze" was the subject of a special study. It does not essentially consist of graphite dragged across the surface but probably consists of an oxide layer. Under certain circumstances it takes polish too.

Figure 5 shows the haze to appear under the same conditions all over the surface with pure, acid-free n-butylphthalate with no crystal boundaries appearing. Figure 6 (ester from paraffin wax) shows haze and crystal boundaries appearing together at higher load with the acid ester (cf. Figure 3). Figure 7, an enlarged detail of Figure 6, shows both haze and crystal boundaries and, by comparison with Figure 2 shows that it is not the haze which conceals the crystal boundaries on Figure 2.

Figure 8 (kerosene), Figure 9 (kerosene + 2% CCl_4) and Figure 10 (straight CCl_4) show the gradual change of the wear print from heavy graininess to bright polish as CCl_4 is added to kerosene. They show: grainy haze (8), appearance of crystal boundaries on adding 2 percent CCl_4 (9) and disappearance of haze with well visible crystal boundaries on lubricating with straight CCl_4.

HAZE MOSTLY OXIDE

Under the conditions of the experiment—access of air, good solubility of oxygen in kerosene—we have to conclude that the haze consists mainly of oxide and that both haze and Beilby layer are dissolved by acid or chlorine action. This appears still more strikingly on comparing Figures 11, 12 and 13, the enlarged details of Figures 8, 9 and 10 respectively. This group of figures conclusively shows that we are essentially faced

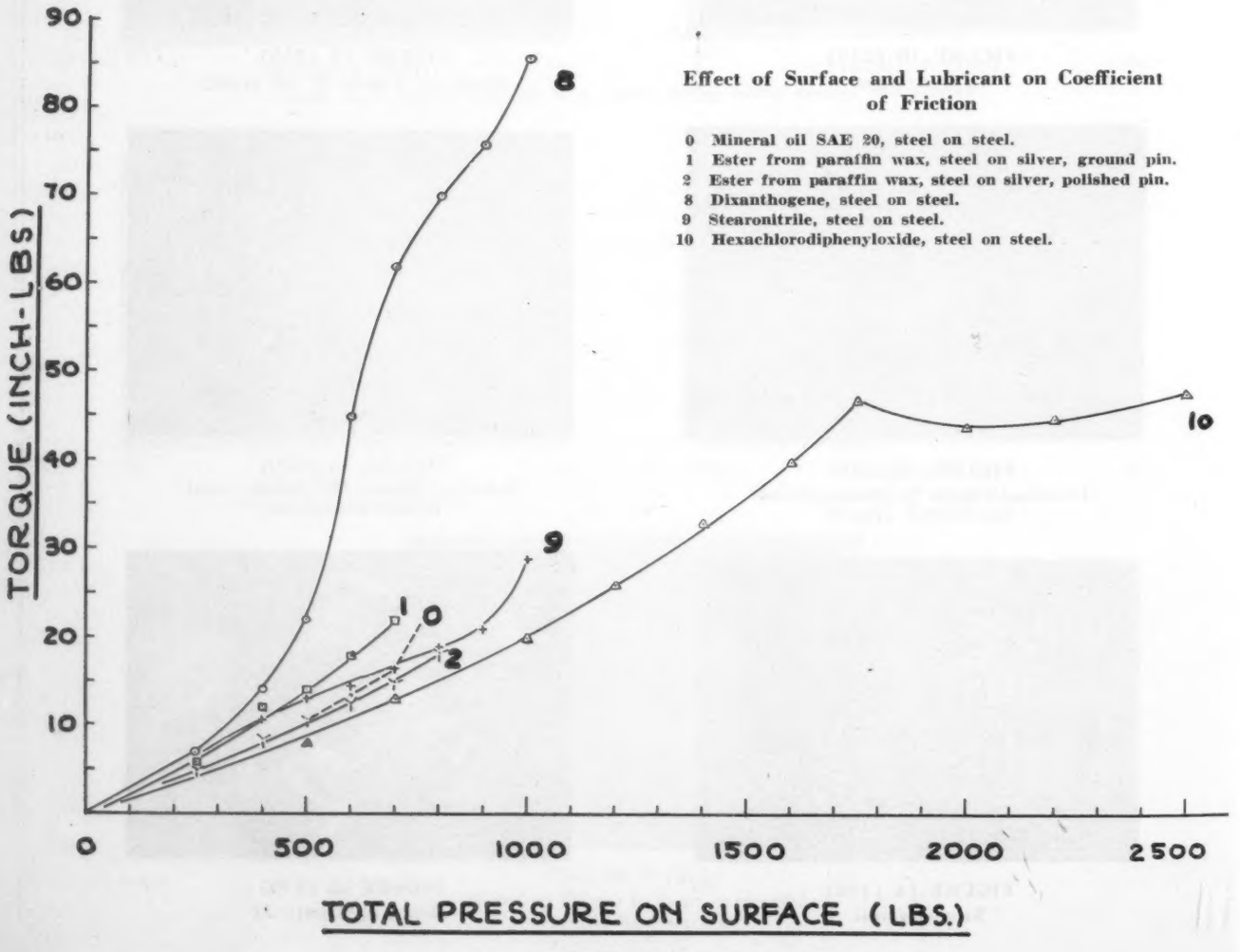

FIGURE 16

with a chemical bulk effect and not an effect of surface orientation.

In conclusion, Figures 14 and 15 show the surface change on lubricating with triamylamine (Falex 563 pounds). In this case the surface quickly assumes an almost uniformly deep blue color, indicating a considerable thickness of a surface compound. The crystal boundaries are still well visible, which is not surprising. The thickness of the layer builds up very fast in comparison with the oxide layer, attacking the whole material at a comparatively low temperature as shown by the very narrow rim of bright polish. Figures 14 and 1 are directly comparable with regard to load and running time and already show the difference in surface reaction.

3. *Torque-pressure—(Falex) curves and the coefficient of dry friction.*—The measurements on seizure discussed in the preceding paper[4] (in the following paragraphs briefly referred to as II-A) have been supplemented by torque-pressure curves for standard steel specimens with various lubricants. The working principle of the machine has been described in the above mentioned paper. On interpreting the curves we have to remember that the experiments start with a line contact between the polished jaws and polished pins. Thus the initial unit pressures are very high. Figure 6 (II-A) shows a photomicrograph of the polished and the commercially ground pin. The seizure values of table 1 (II-A) for oils of different viscosities show that any viscosity effects at these high pressures and local temperatures must be small and practically independent of the lubricant. Finally, the experiments of Hardy and Bircumshaw[6] and of Beare and Bowden[7] justify the assumption that friction in the case of our experiments follows the law of Amontons-Coulomb, according to which we have:

$$\text{frictional resistance } R = \text{coefficient of friction } \mu \times \text{pressure normal to the surface } p$$

In the experiments we measure a torque (force $\times$ lever arm) and the formula assumes the form: Torque/lever arm $= T/a = R = \mu \times p$ or $T = (\mu \times a) \times p$. Writing μ' for $\mu \times a$ and plotting Torques T against pressures p we obtain from the slopes of the curves $dT/dp = \text{tg } \alpha = \mu'$, the coefficient of Coulomb friction multiplied by a constant, the lever arm not being evaluated, as we are interested only in relative values. The coefficient of friction is a characteristic of the surface, depending both on its chemical nature and on its physical condition. Roughness of the surface may result in a higher torque due to the larger input of work into the metal surfaces. Thus both a change in roughness and in the chemical composition of the surface will appear as a change in the coefficient of friction.

Figure 16 (Curves 1 and 2) shows the straight "work" effect with exclusion of chemical changes of the surface on torque-pressure curves of silver jaws against a polished (2) and a ground (1) pin respectively, lubricated with an ester from paraffin wax. The cold rolling effect on the silver in both cases and the filing effect of the ground pin were plainly visible on the specimens. Excessive local temperatures cannot build up due to the plasticity of silver; as the pressure increases the actual bearing area increases and the silver surface stays a silver surface because it is chemically inert to the lubricant. Moreover, silver and steel do not interdiffuse. Curve 0 was obtained for comparison on mineral oil SAE 20 for steel on steel with a polished pin. The curve follows closely curve 2. On curve 0, however, seizure occurred at 700 pounds whereas with silver-steel seizure could not be observed under any conditions and pressures for the reasons explained above. What is important is that the coefficient of friction of curve 0 is during the whole experiment much smaller than for curve 1. This shows that friction in itself has nothing to do with seizure as long as it does not entail other secondary effects, viz., a radical change of surface conditions. The radical change is in this case the disappearing of the oil, metal-to-metal contact and welding (interdiffusion). Curve 0 is smooth and ends in the seizure point. It has a slight upward trend because seizure does not set in suddenly, the pressure on the "peaks" not being uniform.

CHEMICAL CHANGES

The other curves of Figure 16 show examples where the chemical changes of the surfaces are visible by discoloration or by microscopical examination. The experiment of curve 8 (steel-steel and dixanthogene) did not result in seizure at all, as the specimen crumbled and disintegrated. This curve and curve 9 (stearonitrile), showing similar phenomena, are characterized by continuously changing coefficients of friction. The nitration of the steel is not as violent as the formation of the sulfide, the curve ends with seizure, but in an entirely different way than curve 0 of the uncontaminated surfaces. Curve 10 (hexachloro-diphenyloxide) is typical for the chlorine action, again a chemical reaction. The surfaces acquire a high polish, the chlorine dissolving the asperities and thus increasing the actual bearing surface and relieving excessive local pressures and temperatures exactly as in the case of silver, with the difference that in the present case polish is aided by a chemical reaction whereas with silver it is just a rolling effect. At 1800 pounds, due to excessive local heating, evaporation or reaction of the chlorine with substances other than the metal may have taken place. The specimen seized locally and a much smaller bearing area and torque resulted.

Curves 6 and 7 (Figure 17) show the effect of acid which results in the erosion of crystallites and roughening of the surface. The ester methylphenylstearate probably permits the formation of a smooth oxide film. Curves 20 and 40 (methyloleate, commercial, containing acid and pure, respectively) show the acid effect still better. Up to 1300 pounds the curve is the same for both lubricants. Then the curve branches and the acid-free ester shows a considerable lubricating and frictional superiority. The initial coincidence of the curves and their separation later clearly show that these friction phenomena are to a great extent chemical phenomena. What we might call the contamination of the surfaces from the point of view of dry or solid friction, is originally the same in both cases, viz., a condensed film of methyloleate covering a slightly oxidized steel surface as a boundary layer. Part of this primary film is built up by molecules of oleic acid in one case. At 1300 pounds the temperatures at the load-carrying peaks rise so high that the dissociation and reactivity of the acid become perceptible and the surfaces become rough. An increasing number of peaks becomes exposed and welds as the coefficient of friction rises. This rise causes a rise in temperature, exposes more points etc., resulting in a rapid rise of slope of the curve. Curve 40 has a point of inflection as has, perhaps, curve 20.

Two effects are competing in experiment 20: the contaminating, oxidizing effect of the ester on the surface and the disintegrating, dissolving and cleaning effect of the acid. The latter effect increases with increasing temperature more rapidly because its basis is the simple

increase of acid dissociation whereas the process of oxidation involves a process of diffusion into the solid surface. One would expect the thickness of the oxide film to increase. The speed of increase is inversely proportional to the thickness of the oxide film.[8] The thicker the oxide film the less is the chance of local seizure. Therefore we would expect a decrease of our coefficient of friction as the oxide film becomes more uniform, perfect and thicker. This is what we observe on curve 40, incidentally in agreement with Dow,[9] and Fink and Hofmann's measurements on the dry friction of surfaces with increasingly thick oxide films. In a later paragraph we shall see that such decrease of the coefficient may also be due to another cause.

The question whether final seizure occurs will depend on the kind of chemical high-temperature reaction and the physical properties of its products. Polymorphous transformations, dissociation of compounds or other reactions may well result in disintegration of the surface and exposure of fresh metal surfaces or the melting point of the compound may be reached.

TORQUE-PRESSURE MEASUREMENTS WITHOUT CHEMICAL CHANGES

In a preliminary attempt toward a better separation of the various factors determining the coefficient of non-viscous friction the exclusion of chemical reactions with a fair approximation was attempted by measuring torque-pressure curves for silver against polished steel. A motor oil SAE 20 and petrol ether respectively were selected as lubricants of widely divergent molecular size, volatility and viscosity. The curves were followed up to about 30,000 pounds per square inch, the dT/dp values were 0.014 and 0.018 respectively, a difference which is at least partly within the uncertainty of the surface polish of the steel pin. As would be expected there was not a trace of chemical reaction or seizure to be observed due to the chemical inertness of silver, its lack of solubility in iron and the low temperatures due to the yielding of the silver. Experiments along these lines are in progress.

SUMMARY

Summarizing our experiments and their bearing on non-viscous friction, the conclusion appears well founded that the phenomena are, to say the least, closely related to the phenomena of dry friction. Work, appearing as friction, may take the following forms:

1. Work spent in overcoming the resistance of the metal against plastic deformation (slip and crystal twinning). This work is characteristic of the individual metal and must be related to the lattice forces.[11,12]

2. If a chemical compound forms at the surface, which is probably the rule, this compound will be orientated on the surface and in many cases will increase in thickness by diffusion, e.g., copper in air or oxygen.[9,10] If the strength of the newly formed material is greater than the strength of the metal (or its tendency to slippage smaller), the compound layer will, on removal by friction, adhere to the metal, thus exposing a fresh metal surface with smaller friction. This has been accomplished with copper in an oxygen atmosphere by Fink and Hofmann.[10] The degree of uniformity of the frictional coefficient observed in this stage will depend on the regularity of formation of the layer of the compound. With the alloys commonly used in engineering practice, e.g., cast iron and steel, that is to say with chemically inhomogeneous surfaces, in many cases a varying and increased value for the coefficient of friction will result due to considerable roughening of the surface entailing ordinary interlocking of irregularities. We find this effect very pronounced on the torque-pressure curve for dixanthogene in accord with certain observations of Beare and Bowden.[7] Another type of fluctuating friction, or perhaps seizure in steps, has been described by Fink and Hofmann[10] and Bowden and Leben.[13] This phenomenon appears to lend itself to an explanation on the theory of elasticity. On applying a normal force to a conglomerate of crystallites those whose planes of slippage happen to lie at an angle of 45° with respect to the normal are the first to yield (see Tammann, loc. cit. p. 60). From this it follows that the resistance to slip of such a conglomerate must necessarily vary as a

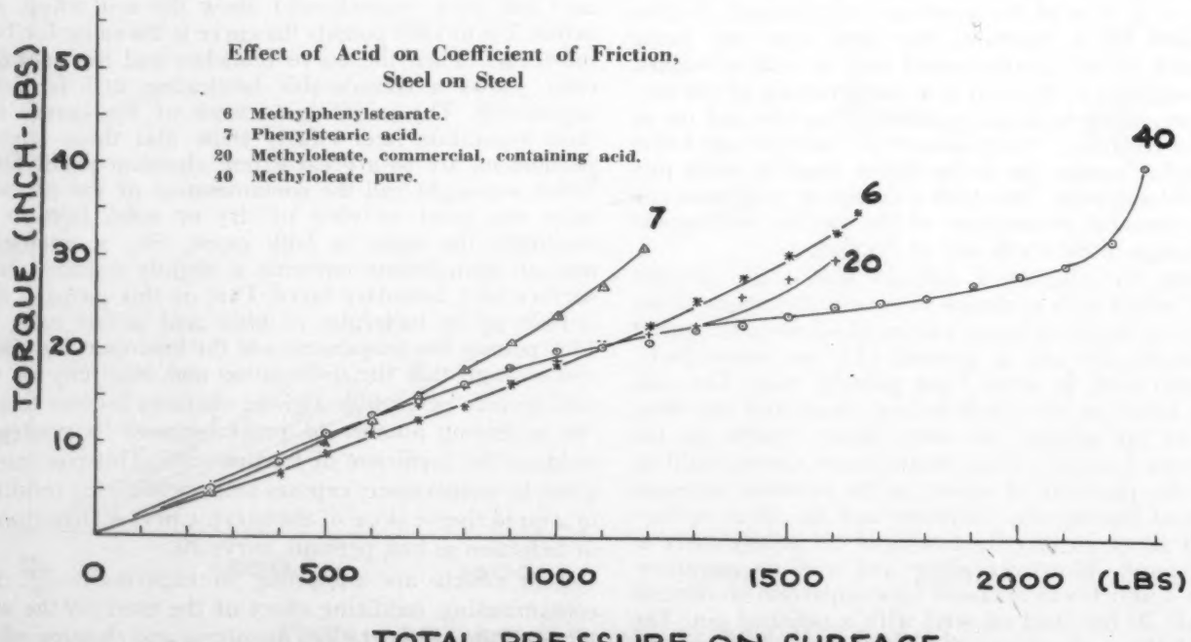

FIGURE 17

measuring device passes from one crystallite to the next. For an illustration of this phenomenon of orientation and slip, familiar to the metallurgist, the reader is referred to the book of Nadai, p. 31.

It is realized that the preceding discussions on Coulomb friction are necessarily of a phenomenological and qualitative nature. However, the enormous differences, sometimes amounting to 1:40, between the coefficients of friction of contaminated and clean surfaces justify the presentation and discussion of experimental material on the process and the nature of such contaminations. They point moreover the way to the exclusion of that factor and to a better definition of the nature of the surfaces, including the various roles of adsorption layers, thus, serving to bridge a gap between purely physical[14] and engineering research in this important field.

The author wishes to acknowledge loan of equipment and material by the Research Department of the Union Oil Company of California.

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Oil Filters *and their Effect on the Lubrication and Wear of Engines**

JAMES E. HURN
DeLuxe Products Corporation, LaPorte, Ind.

WE will make no distinction between industrial and farm operations in this paper, although tractor manufacturers have generally made such distinction in their equipment. The load factor would be the only difference that would affect lubrication. The farm tractor operates continuously and at lower BMEP while, with industrial tractors, the load varies with the operation and we must assume that, fundamentally, a properly-lubricated piece of machinery should show no wear. However, in modern high-output engines excessive heat and its effect on the lubricant must be considered.

Modern engineering practice requires that a tractor be equipped with adequate air cleaners for carburetors, oil filler pipe and crankcase breather to prevent foreign impurities from reaching the motor. Most air cleaners today, if properly serviced, fulfill this requirement. But, many tractor manufacturers also supply an oil filter or strainer on their engines, believing that to remove foreign contamination from the motor is all that is desired and not realizing that it is the impurities formed by the oil itself which must be removed for efficient lubrication. Should the manufacturer feel that a so-called full-flow strainer is required to remove the impurities that get into the oil by careless maintenance methods, this full-flow strainer should consist of a fine screen of large area on the inlet side of the oil pressure pump, or a floating oil inlet to the pump, because no full-flow filter will give protection when the oil is cold or when it has become partly coated.

The modern oil filter should maintain the oil as a satisfactory lubricant. Of course, improved ventilating systems aid materially, but the lubricating ability and the elimination of deposits in a motor is the determining factor of a satisfactory lubricant for the prevention of engine wear.

By checking various types of engines and their lubrication, we can usually determine, by the condition of the oil filter, the lubrication and wear characteristics of an engine. A filter which shows sludge accumulation in it has not fulfilled the requirements as far as correct lubrication and reduction of engine wear is concerned. Either the filter has been improperly applied to the engine or the capacity of the filter is inadequate. Excessive cylinder wear, ring wear and even bearing failures are, in most cases, the result of incorrect lubrication.

The usual test for determining the lubricating value of an oil has been by determining the percentage of solids, carbon, soluble materials and the neutralization number by an analysis, but this is not enough to indicate a satisfactory lubricant. A complete analysis which will indicate the amount of nonlubricating deposits the oil will form in the engine is necessary. Our method of determining this is an analysis for moisture, corrosive compounds and asphaltenes, as these materials are directly responsible for engine wear, through formation of either sludge or lacquer. A filter functioning properly should remove these materials, so that sludge or lacquer will not be found in the motor or in the filter. If sludge and lacquers are allowed to build up, as the result of asphaltenes remaining in the oil, they deposit on the closely fitted parts of today's engines, preventing proper lubrication and resulting in wear. While these lacquers are not hard, they are hard enough to act as an abrasive, starting wear which

*Before the National Tractor Meeting of the Society of Automotive Engineers, Milwaukee, September 28 and 29, 1939.

often times causes adhesion of metals and consequent scoring.

In the automotive industry, the formation of lacquer in high-output engines is a serious problem. We had the opportunity of cooperating with a well-known university laboratory on tests relating to lacquer. The results of these tests proved conclusively that the proper application and capacity of filter removed the asphaltic material from the oil so that lacquers could not accumulate in the motor, eliminating the usual failures.

Our experience has taught us that in order to prevent this formation in the engine, asphaltenes must be separated from the lubricating oil as rapidly as they are formed and while still in the liquid state. This required tests to determine at what point the asphaltenes became more viscous than the lubricating oil, since they are known to increase in viscosity as the oil temperature rises. It was found that if temperature was applied to an oil, reducing its viscosity to approximately 100 seconds, Saybolt Universal, the asphaltenes could be separated. Therefore, the correct viscosity oil must be used, according to engine and operating temperatures. No strainer will separate these impurities formed in the lubricant and which will soon deposit in the motor to become the direct cause of wear. It is very obvious that an absorbent filter must be used.

We are convinced that a recommendation for an oil change after a specified hourly period is antiquated unless the correct application of filters is taken into consideration. The dirt, the load, the fuel and the quality of oil govern crankcase changes. Some oils which operators use are not capable of remaining a satisfactory lubricant for the hours specified by the engine builder. On the other hand, there are many oils used today which are capable of remaining satisfactory lubricants for many times the hours specified by the engine builder. With the variations that exist in lubricants and operations, oil changes become guesswork without the visual aid of properly applied oil filters. Some manufacturers also specify that certain lubricants are necessary for the successful operation of their engines. Possibly they would be correct if they indicated quality and stability in these specifications, but no such factor is included.

We recently had the privilege of assisting in a test with a fleet of tractors, for which a definite brand of oil was specified by the manufacturer and where straining equipment for purifying the oil was used. The operator experienced .017 cylinder wear, as well as bearing failures, in 1000 hours of operation. The same fleet of engines was rebuilt to original specifications; operated on an entirely different type of oil than the engine manufacturer specified, but of satisfactory quality, and with different filtering equipment, both as to application and capacity. It was found after these engines were again operated 1000 hours with no oil changes, that the greatest cylinder wear was .002 with no ring sticking or bearing failures, and no impurities of any sort were found in the motor.

Another group of engines of entirely different manufacture, greatly over-loaded in a particular operation, experienced .027 cylinder wear in 2500 hours operation. Again by using the right viscosity of lubricant, proper ventilation and absorbent filters, these same engines operated 2700 hours with .002 cylinder wear and no oil changes. Of course, in both instances quality oils, of the correct viscosity were used. Had oils of inferior quality been used, more frequent oil changes would undoubtedly have been necessary. We believe, too, that even if good oil had been used with the old-fashioned straining methods, oil changes would have been necessary.

The cost item of satisfactory filtering equipment has always been the predominating factor. Of course, the greatest saving to any operator is the reduction in motor maintenance through the reduction of wear, but is rather intangible so far as definite figures are concerned. However, if satisfactory filtering equipment is supplied, of adequate capacity, the savings which result from this filtering equipment can be immediately accounted for through oil savings. A typical example of this is a fleet of fuel-injection engines using average commercial oils at a cost to the operator of approximately 40 cents a gallon—each engine holding 6 gallons. These engines were successfully operated for 180 hours, the oil kept clean and in perfect lubricating condition for the entire period at a total cost for filter service of $1.56. The engine manufacturer had specified a 60-hour oil change, which, with 6 gallons every 60 hours would have meant 12 gallons of oil at 40 cents a gallon, or a total of $4.80 of oil cost against $1.56 filter service. The above figures are based on an oil and filter change at 180 hours. However, the oil was in perfect condition and fit for further use. Again we state that these savings are dependent upon the proper capacity of filter and the proper application of the filter together with the use of good oil. Had this operator used a poor oil, the filter life would have probably been 100 to 120 hours in which only one oil change would have been eliminated. By assuming that the operator paid 25 cents a gallon and used 6 gallons, it would have meant $1.50 saving on oil against $1.56 cartridge cost, but we are sure that under these extreme conditions, he certainly would have experienced more than 6 cents saving in maintenance.

Under all conditions, we believe that an application of filters which will maintain a satisfactory lubricant is a definite advantage, both to the engine builder for protecting the reputation of his product and to the operator from a financial standpoint.

More and more engine manufacturers, dealers and operators are realizing that transparently clear, clean oil is possible. Yet tests have proven that apparently clean oil can contain those contaminants which will deposit as gums and lacquers, therefore we have assumed that the type of absorption filtration to be used was the type which would remove these contaminants before they could deposit and contribute to wear.

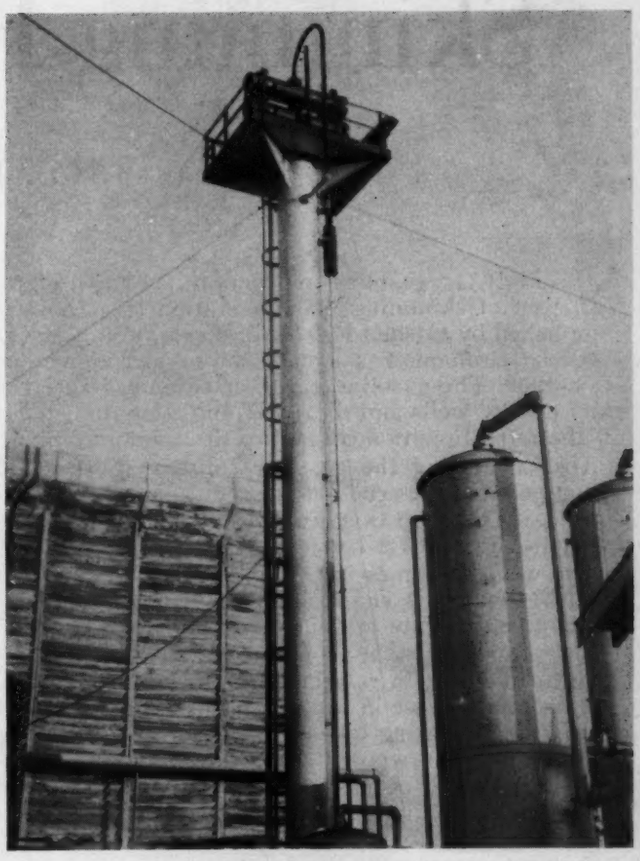
In supplying the correct capacity filter for an engine, it is absolutely necessary to know the characteristics of the engine and, if necessary, to conduct tests to determine them. Fuel contamination from the combustion chamber, as well as the characteristics of the engine, as it relates to oil breakdown in the crankcase, must be correlated, and on this correlation, will depend the flow specifications and capacity of the filter. Very often, when this has been determined, it has aided the engine manufacturer in improving the engine design to produce a motor which gave better operating efficiency from both the oil and fuel standpoint.

Insulated Reflux Condensers in Stabilizer Operations

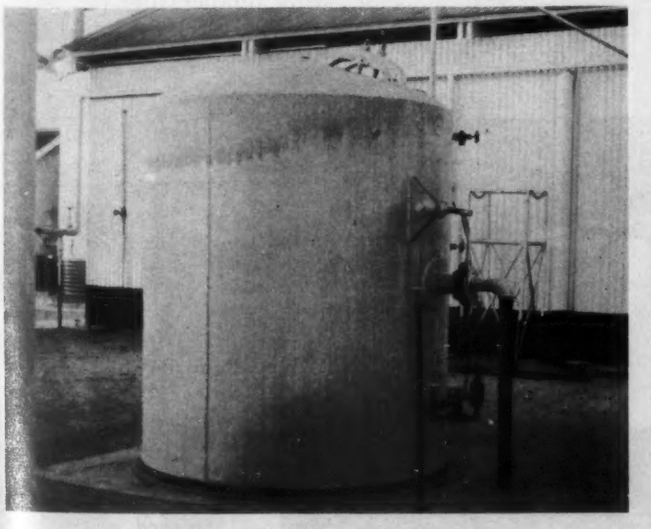
WHEN Gilmore-Dabney, Inc., installed fractionating equipment in its Signal Hill gasoline plant, no thought was given the effect of temperature changes on the overhead reflux condenser sections. Shortly after operations began, it was noted that if the weather was mild and uniform in temperature, the reflux section cooling water circulation was practically constant, and the product removed from the base met specifications without change in composition. If the temperature dropped suddenly, the column became flooded with reflux which caused the finished product to go off specification.

It was decided to accomplish two operations on the stabilizer; both of which have been of inestimable aid in operating the column. One included the installation of a closed water circulating system for cooling the reflux condensers; two of which are used and installed on a structure above the column with atmospheric sections placed in one of the water cooling towers with a surge, or supply tank from which the pump takes suction. The other included complete insulation of the condenser sections, shell, heads and connecting lines with sufficient material to counteract atmospheric effect of rain or cold weather.

The water circulating system required only the use of water cooling sections and the surge tank, above the material already in use, as a pump was set originally to control the volume of water necessary to obtain required fractionation of raw gasoline in the process of stabilizing to marketable grades. The water used for this closed system is obtained from pump exhaust condensate, free of lubricants, and pumped into the surge tank in volumes sufficient to make up for leakage and natural loss. The surge tank is equipped with an internal float connected to a valve on the water make-up line, which maintains a constant level in the surge tank at all times. The line feeding make-up water leads from the boiler-feed pumps, which handle only treated and condensed water, free of scale forming minerals and oil.



Fractionating Column



Surge Tank

In the two years that this installation has been used it has not been necessary to enter the reflux cooling sections, and no noticeable drop in efficiency has been observed. A reverse manifold was installed at the time of the added improvements, which permits a stream of water, at high velocity, to be passed through the tubes to clean out soft sediment that might be deposited in the tubes, but this process has not been practiced frequently; which leads one to believe that adequate cooling is being obtained with this system in use.

Graphs and records kept in the office of the gasoline plant show that temperature fluctuations are rare in the overhead conditions of the fractionator, indicating almost a straight line temperature curve of day-to-day operation. This was not accomplished prior to the installation of the condenser sections.

Natural Gasoline Production

Synchronized with

Skimming Plant Operation

J. C. ALBRIGHT

NATURAL gasoline extraction as an integral part of skimming plant operation has been accomplished by Cosden Petroleum Corporation, whose unit near Graham, Texas, has been in operation since May, 1939. The gasoline absorber column draws gas from nearby wells and the absorbing medium is a cut off the refractionation column of the skimming plant.

After collecting the gasoline content, the rich oil is pumped into the crude oil charge to the pipe still so it can pass through this heating unit and into the refractionating unit for conversion into motor fuel.

The wet gas comes into the absorber unit at field pressure, which is sufficient to deliver the dry gas to the pipe line gate of the distributing company.

The skimming plant proper is flexible in operation, since an increase in raw material charging temperature and an increase in the amount of reflux delivered to the refractionating tower allows cuts of lubricating oil stock to be drawn off at the bottom.

Principal units of this plant are the tube still, the fractionating column, a stream-treating system and the gasoline absorption unit.

Young County crude, 42 A.P.I. gravity, is charged direct to the tube still heater. Both a steam-driven reciprocating pump and a motor-driven centrifugal pump are provided, one being used while the other remains for emergency.

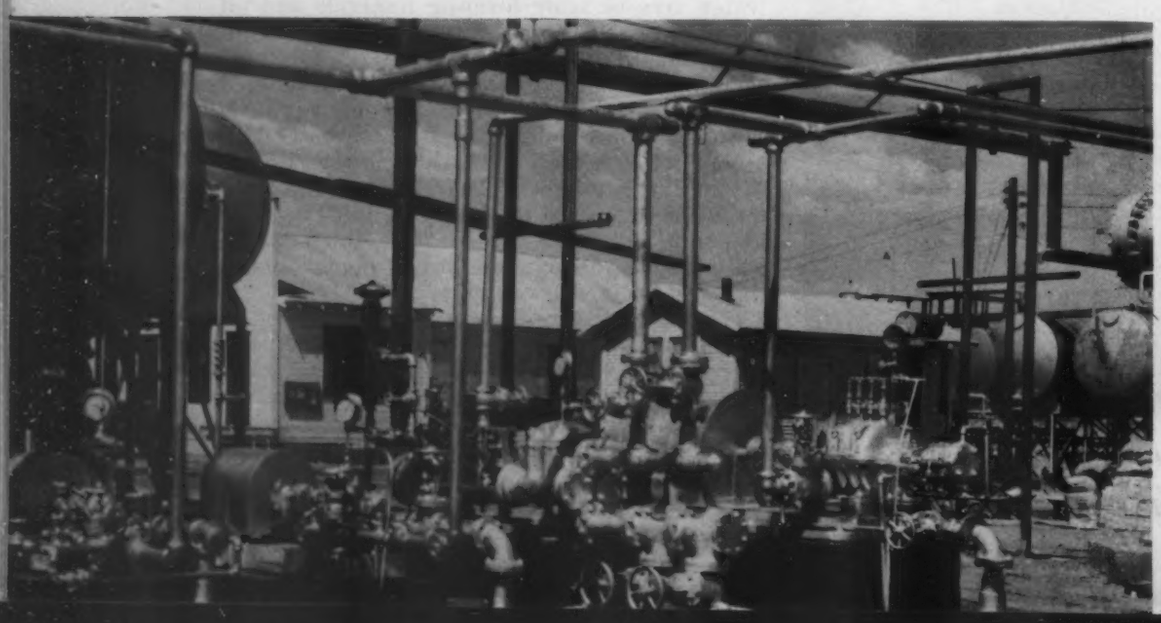
The rate of flow through the plant is controlled to obtain a uniform processing rate and the pressure maintained on the discharge of the feed pumps is held at 50 pounds, sufficient to deliver the crude through the heater and to the fractionating column at the rate desired. Through convection and radiant tubes the charge passes while being heated, under ordinary operating conditions, to a transfer line temperature of 575° F.

FRACTIONATION METHOD

The transfer line carries the processed material to the fractionating column where it enters below the bottom bubble plate. The column is 6 feet in diameter, and 60 feet high, containing 14 trays, which serve for fractionation only. Process steam is introduced into the chamber below the bottom tray to facilitate distillation, which is varied in quantity as the operation of the plant is changed from ordinary to special.

Changes in operation are made to produce special cuts, mainly from the bottom fractionating plates, and to convert the residuum in the chamber below the fractionating trays from industrial fuel oil to steam refined cylinder stocks, with a cut of lubricating oil removed from the bottom draw-off section. The normal operation cycle is employed when industrial fuel oil is produced as a bottom cut, and the various products, such as gas oil, distillate, kerosene, naphthas and gasoline are manufactured.

When normal operation is carried out the transfer temperature held at 575° F. and the column is operated with a vapor outlet temperature of 290° F. maintaining this condition with reflux pumped from the straight-run gasoline accumulator drum to the

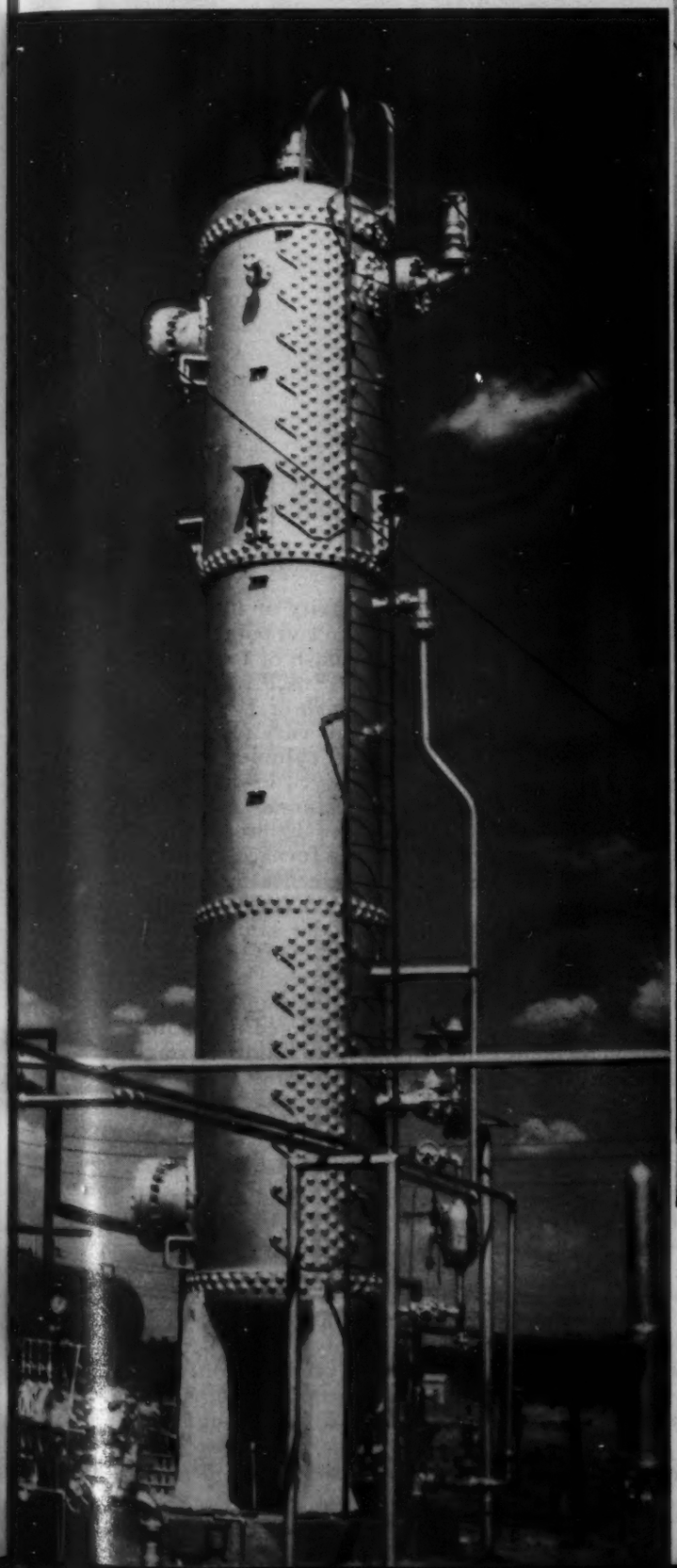


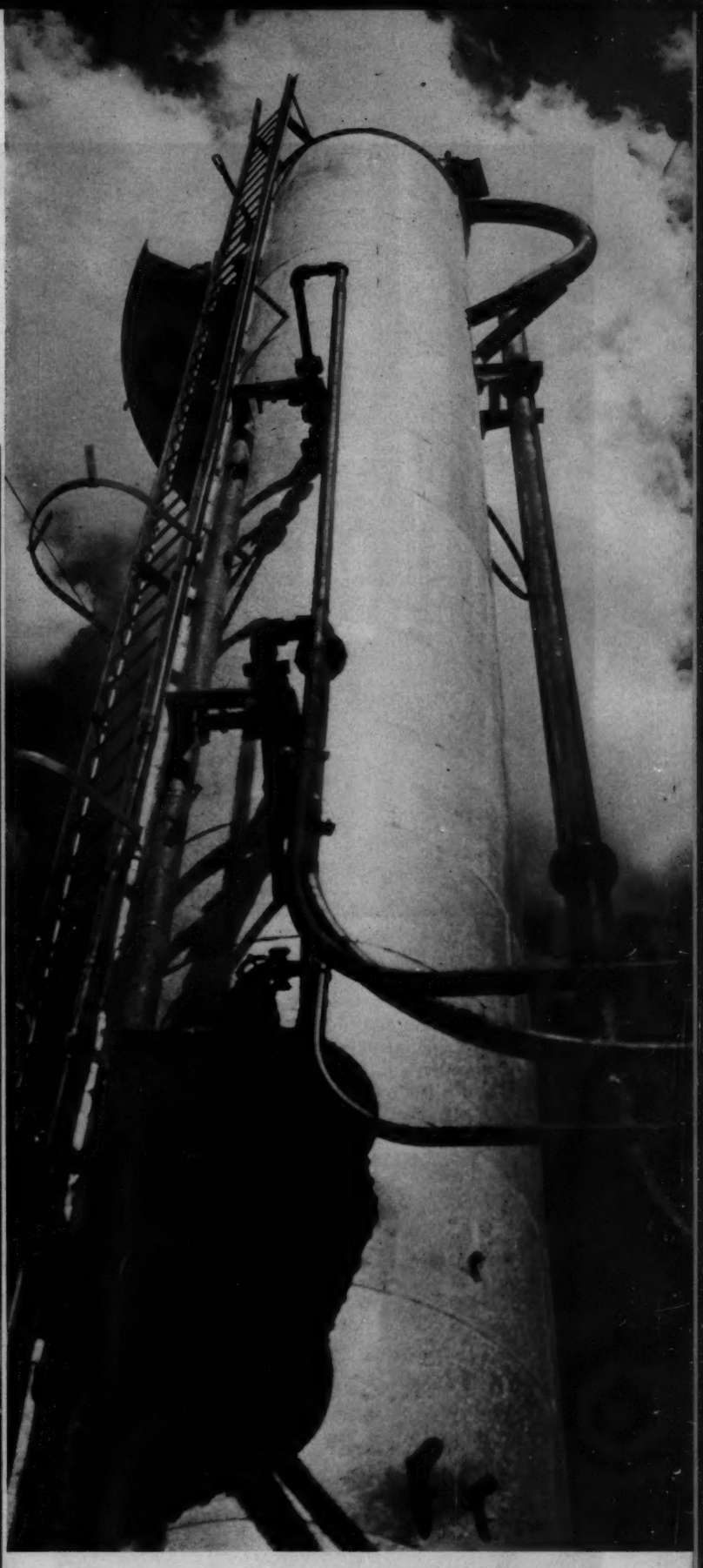
Both steam and electric power are used for pumping, with units set in the open. This battery handles raw material charge, reflux and finished materials.

A side cut off the skimming plant column (right) is detoured to the natural gasoline stabilizer (below) to serve as mineral seal oil.

The enriched cut then enters the still with crude oil charge stock and gives up its lighter fractions in the skimming plant cycle.

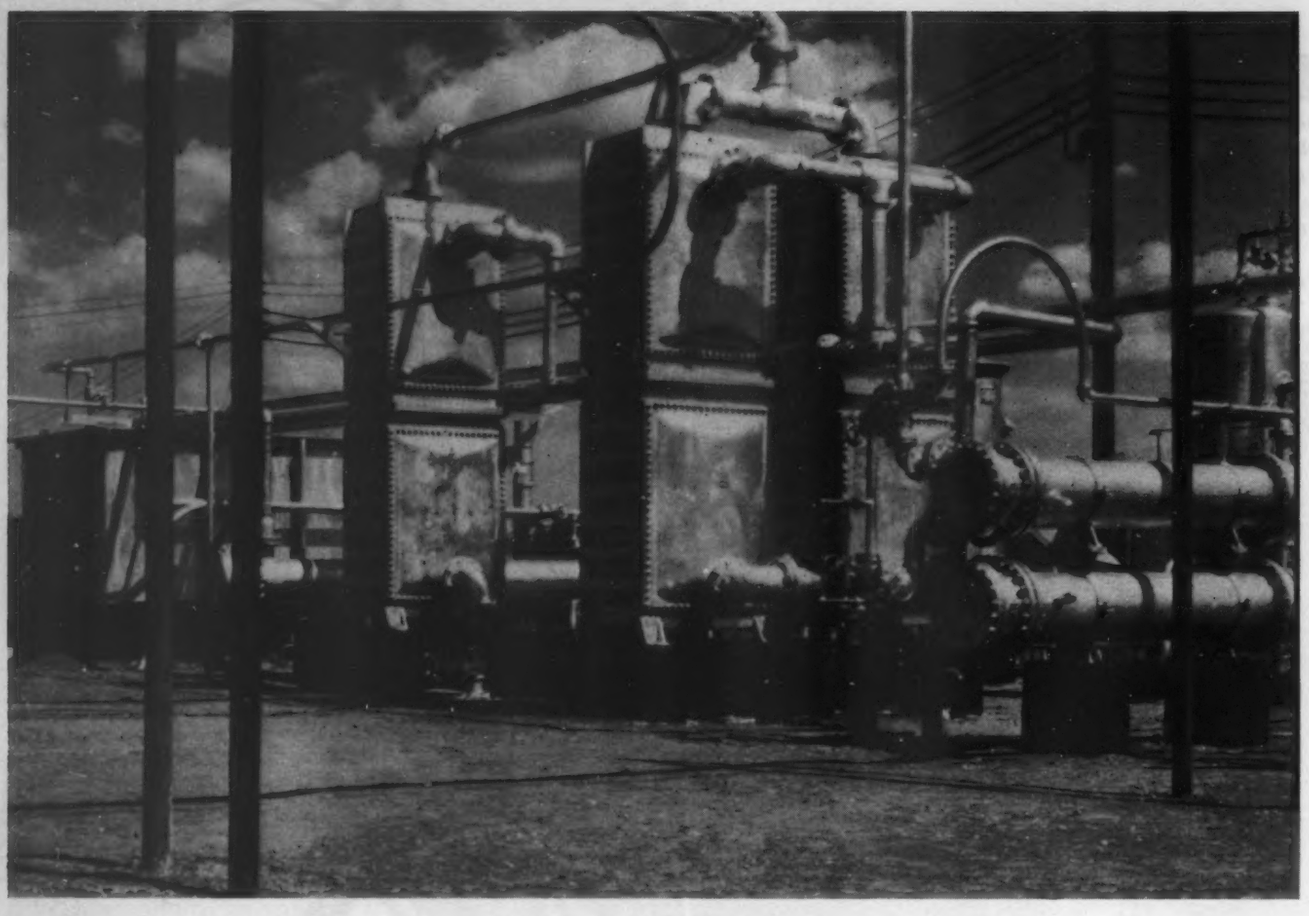
Natural gas comes into the absorber at field pressure.





By stepping up the temperature in the pipe still furnace and increasing the amount of reflux pumped into the tower (above), fractionation may be so changed that the bottom cut is a steam refined cylinder stock and a cut of lubricating oil.

This is a special operation of operating the skimming plant of Cosden Petroleum Corporation near Graham, Texas.



Condensers and after coolers.

top of the column in volume sufficient to keep the end point of the gasoline at or near 400° F. When operating for special products, the volume of reflux is increased to prevent the column from producing a higher end point gasoline. The gasoline produced from Young County crude has the following distillation:

WHITE MOTOR FUEL

Gravity	59.5° A.P.I.
IBP	105° F.
10 percent	170° F.
20 percent	200° F.
30 percent	220° F.
50 percent	260° F.
70 percent	290° F.
90 percent	360° F.
End point	404° F.
Recovery, percent	98.0
Color	30
Doctor	Neg.
Corrosion	O.K.

Kerosene manufactured in the column has the following distillation:

KEROSENE

Gravity	42° A.P.I.
IBP	368° F.
10 percent	407° F.
20 percent	422° F.
30 percent	433° F.
50 percent	442° F.
70 percent	462° F.
90 percent	503° F.
End point	525° F.
Color	30
Doctor	Neg.
Corrosion	O.K.
Flash	125° F.

A light distillate having a gravity of 40° A.P.I., an initial boiling point of 320° F., an end point of 575° F., a Saybolt color of 10-20, and a flash of 120° F. is also made. The straw distillate is 37° A.P.I. gravity and has a color of 4 NPN with a flash of 175° F. and an end point of 650° F. The bottoms vary from standard industrial fuel to steam refined cylinder stocks, depending upon the method employed in operating the furnace and the fractionating column.

When the refinery is operated to produce refined bottoms, the temperature of the furnace is increased so that the transfer line is between 675 and 680° F. The column, after the material reaches it from the furnace, is controlled in much the same manner as when the plant is being operated in the normal manner. The amount of reflux is increased to control the end point of the overhead stream of straight-run gasoline, and the side cuts are changed in distillation range. The plant is not equipped to follow through on lubricating oil clarification, dewaxing and further refining, and the special operating conditions are seldom used.

TREATING ON TRANSFER LINES

Normal operation produces a residuum specially adaptable to cracking. Therefore, the bulk of this product is shipped to the cracking units at Big Spring where it is blended with the Howard-Glascock crude bottoms and cracked into a high-octane fuel.

The streams of straight-run gasoline, kerosene and the special distillates contain only a small percentage of sulphur compounds, as the crude produced from wells in this part of North Texas is comparatively sweet. Facilities are included in the design of the

plant to treat these products as they are manufactured, by affording contacting vessels for caustic washing in the stream from the accumulator drums as they flow to run-down tanks.

For the straight-run gasoline, a single vessel is operated, installed in the open on a concrete pad, and resting upon a low steel structure for support. The gasoline flows through liquid controllers to this vessel into which a solution of caustic is continuously pumped. Similar vessels are provided for the kerosene and distillate cuts which are operated in substantially the same manner as the one provided for the straight-run gasoline.

The yields of the plant when operating on Young County crude are as follows:

YIELDS

	Percent
Straight-run gasoline	41.0
Kerosene	3.5
Distillate	13.5
Gas oil	0.7
Lube oil	1.7
Industrial fuel oil	39.1
Gas and loss	0.5
Total	100.0

On leases in which Cosden Petroleum Corporation is interested, there is a considerable volume of natural gas, not associated with the oil-bearing formation, but produced from wells drilled into a different sand. This gas is delivered, in part, to gas transportation companies, and in part is used as refinery fuel. The gas companies desire this fuel to be free of hydrocarbons which ordinarily would condense in transportation lines and collect as drips.

NATURAL GASOLINE ADJUNCT

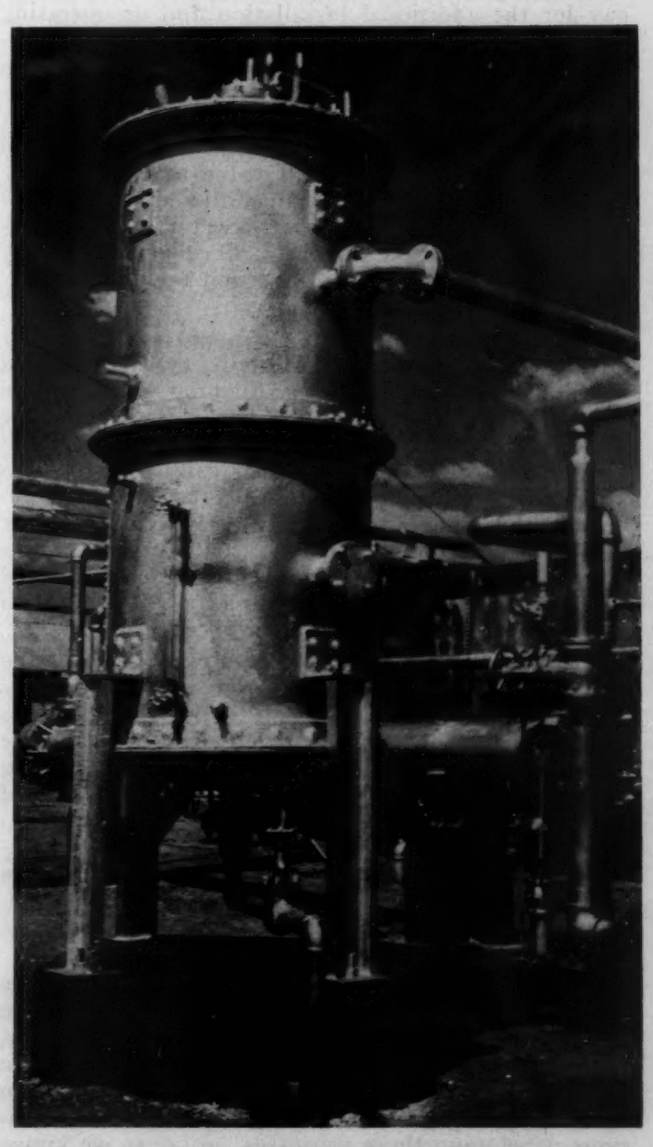
To remove these hydrocarbons, and also to provide a product which will blend with the straight-run gasoline to control the front-end volatility, a high-pressure absorber was installed in the refinery, set near the main distillation column. Well pressure is sufficient to deliver this gas to the high-pressure absorber, and to pass it onward from the plant to the measuring stations at the pipe line terminal.

This plant is closely tied in with the normal operation of the refinery, and is dependent entirely upon the operation of the fractionating column and crude heater for its operation. A cut from the side of the main fractionating column, similar in specifications to mineral seal, but which is usually recovered as a straw distillate, and upon condensing and cooling is pumped with a high pressure, motor-driven, centrifugal pump to the top of the high-pressure absorber. The temperature of this distillate, under usual operating conditions, is sufficiently low that it is not necessary to pass it through after-coolers before use in the absorber.

The amount of distillate delivered to the column is such that all of the required, higher-boiling hydrocarbons, such as Nbutane and heavier are removed from the gas. The object is to obtain a low-vapor-pressure natural gasoline, and to prevent obstruction of pipe lines with easily condensed fractions in the gas. The passage of gas is directly from the field gathering lines, through the absorber, a residue scrubber, and then into the mains of the gas transportation systems.

The absorption oil travels in conventional flow from the top to base, and is controlled in flow with a liquid level controller installed on the lower section of the column. By remote operation, the absorbing medium is pumped to the column in relation to the amount contained in the base of the absorber. Pumping from the base of the absorber is not required, since the pressure is much higher than any pressure encountered in the operation of the refinery.

To recover the absorbed gasoline from the absorbing medium, the stream of rich oil is piped to the inlet of the crude charge heater, so that it will mingle with the crude as it passes through the heater and to the fractionating column. Venting of lower-boiling fractions is not required, since the gas is handled through the absorber in such manner that selective absorption is obtained. With the return of the distillate cut, carrying the absorbed gasoline, to the fractionating column, the natural gasoline thus obtained is blended while hot and in the vapor stage with other refined vapors, and condensed with the straight-run product from the vapor outlet at the top of the main column. The absorber may be operated as a gas stripping unit, or may be removed from connections with the refinery by closing off the stream of absorbing oil, all or either without materially affecting the efficiency of the refinery in any manner.



All treating is done while material is under transfer. This unit is for caustic washing on stream after condensation while straight run gasoline is enroute to run down tanks.

Catalytic Cracking

A Review and Analysis of Future Trends in This Phase of Refining

ARCH L. FOSTER
The Lubri-zol Corporation

THE question of the adoption or rejection of a process for catalytic cracking or catalytic reforming resolves itself in its most fundamental aspect into the question: Will the process give a product the extra yield and superior quality of which will pay for the additional installation and/or operating costs involved? Will the premium value of catalytically cracked or reformed motor fuel, considered as the mathematical product of its yield times its octane-number-blending value be greater than the corresponding results from a thermal-cracking unit, and will this increase in over-all value of the catalytic product be great enough to cover all additional costs? Unless these questions can be answered in the affirmative with reasonable certainty, no refiner can justify the decision to build a catalytic unit for either cracking or reforming.

The possibility that in the near future greater strides may be made in catalytic cracking is not necessarily an excuse for postponing the adoption of this type of process. Since data already available indicate with a reasonable degree of certainty that at least in a number of instances catalytic processes are proving efficient economically as well as technically, there is no reason why an individual refiner if he can determine with fair accuracy that such a process will give net returns comparable to thermal operating results, should not undertake the effort of applying the method to his own operations.

So far as we can see now, catalysis is one of the "coming things" in refining. Even more obvious is the apparent fact that the catalytic process of 5 years from now will be much more efficient than any we know today. Burton did not stop building cracking stills because he could not process 20,000 barrels of charge daily, to yield 70 percent or more of 70-75-octane gasoline. The decision now on catalytic cracking must be based on the answers to the questions asked in our first paragraph, applied to the individual refiner's situation and to his own peculiar requirements.

At present the primary limitation, technically speaking, appears to be that of size of installation. Houdry Process Corporation officials, for example, are not yet willing to attempt to apply catalysis to small installations in this country. No minimum charge capacity has been set by any of the organizations developing these processes, so far as we know, but a minimum of 5000 barrels of charge per day has been mentioned by some technologists as the lowest that may be expected to "pay out." This figure, even if correct now, will doubtless be reduced as time goes on, just as was the case with thermal-process development. Nor are we willing to commit ourselves to this or any other figure. If those engineers most conversant with catalytic cracking are uncertain as to

CONCLUSIONS

If we may draw conclusions from the facts presented here, they must be general. Too little is known of the ramifications of catalytic cracking and reforming now to make wide generalizations safe or sane. However, the following statements appear to be warranted by data available on these processes and their products.

1. Catalytic cracking as now practiced appears to be suitable economically for the larger capacity installations, in the larger refineries. The lowest unit capacity which is practicable has not yet been determined, but its size will be greatly reduced during the next two years, from those larger units now in successful operation.

2. Catalytically cracked gasoline, with a blending octane value of 90 or higher, has a premium value of more than 1 cent per gallon, or 47 cents per barrel, as a conservative estimate, from which the refiner can pay extra costs of operation. This premium valuation is based on octane number improvement by lead saving alone, and does not include other possible advantages which may accrue from other properties of the product. Nor does this evaluation include the added value of the gas oil which may be produced, reputed to be a first-grade charge stock for thermal cracking.

3. Catalytic reforming, or dehydrogenation, of low-grade gasoline and naphtha appears to offer a means of fuel improvement and saving in refining costs which is more immediately available to the average-to-small refinery, at a comparatively low cost and long plant and catalyst life.

4. Manufacture of special, extremely high-quality fuels has been made practicable for the refiner who is interested in that field, by the application of both thermal and catalytic processes.

5. Catalytic desulfurization for improvement of octane number and for a remarkable increase in lead susceptibility has been perfected by two processes to a point where the average refiner handling high-sulfur products may apply it economically to his stocks to affect an important saving in over-all fuel cost.

6. We still need to know so much more about catalysis in refining that the technologists will be extremely busy—from now on.

Presented before the thirty-ninth annual meeting of the National Petroleum Association, Atlantic City, New Jersey, September 14, 1939.

the crucial point in unit size where the law of diminishing returns functions unfavorably, we know of no others alive who are in position to determine that point.

RECENT DEVELOPMENTS

Before discussing more recent developments, and the details of catalytic cracking results, let us have a look at the present position of catalytic processes. Recent published figures show that 15 Houdry units are operating, under construction or design, with a reported total crude capacity of 228,410 barrels per day, and charging to the catalyst cases about 150,000 barrels of reduced crude or other crude fractions. Twelve of these units are in the United States, and are capable of charging to the catalyst case about 132,000 barrels per day. Two units are in France with a case capacity of about 15,000 barrels; one is in Italy which charges 2600 barrels of gas oil daily. The number of units built which operate other catalytic processes is not known with certainty, but Phillips Petroleum Company, Standard Oil Company of Louisiana, Shell Oil Company are among the number which have been reported by rumor to have built or to be building such units. It is estimated that at least 300,000 barrels of crude per day can be charged to catalyst units in this country and abroad. No data are available to show how much crude is now actually being processed by these methods.

At least one school of engineer-executives believe that catalytic cracking will find its place, not necessarily in the making of higher octane numbers, but in making competitive gasoline more cheaply, if it is to fit into the economic technology of refining. Catalytic cracking of heavy oils, they say, cannot make as advantageous a boost in octane numbers as can catalytic reforming. Cracking with catalysts, however, has two distinct and undeniable advantages; it can produce a higher yield from the crude than can thermal processes, and it can if necessary produce higher-octane products to make or meet competition, either by cracking or reforming or both. It must fit into the general cracking plan of the refinery, to do a job better and more cheaply than any other method can do it, or it must produce a product which no other process can make. Asked if he would install now a catalytic cracking unit in a refinery if he were operating one, one of our best engineering executives told us recently, "I would not built a catalytic-cracking unit now, to replace serviceable modern thermal capacity now operating; I could not afford to overlook this new process if I were building additional cracking capacity for my refinery." While this statement is not presented as a consensus of the opinions of all engineers qualified to hold opinions on the matter, it gives food for thought, and indicates the undeniable importance catalytic cracking will probably hold in future refining operations.

CONTINUOUS OR INTERMITTENT

One group of engineers developing catalytic processes have decided that in the present state of the art no economic advantage can be shown in catalytically cracking charge stocks of the light-gas-oil type. Because of higher yields of higher-octane product, cracking heavy gas oils does, however, show advantages, especially if the balance in the refinery's operations is such that a unit of economic size can be used for this step.

We now have two types of catalytic cracking and/or reforming processes—the intermittent type which has been applied commercially almost exclusively so far, and the continuous type. One unit of 1500 barrels charging capacity is now being operated as a continuous process, and those acquainted with the results obtained are convinced that within one to two years all catalytic cracking, by whatever process it is operated, will be of the continuous brand. In this process catalyst and charge—the latter in the vapor state—are brought into contact continuously, the cracked vapors are removed "overhead" so to speak, and the catalyst passes from the contact chamber continuously to be regenerated outside in any practicable manner, while fresh catalyst enters the reaction zone, also continuously.

We are informed that 40-60 percent of the installation cost of the intermittent unit is for equipment and procedures involved in the revivification of the catalyst, in place. We are also told on what we consider unimpeachable authority that a continuous cracking or reforming process can be built for 60 percent of the cost of an intermittent unit. If we assume that the ratio of these costs may remain approximately the same, no matter how the actual cost figures of either process may be reduced as time goes on, the continuous process has inherently a heavy advantage.

Catalytic cracking of residual oils has not yet become a commercially feasible undertaking, in the opinion of many qualified engineers. The deposition of carbon from even the cleanest residual stock is of the order of 15 percent, we understand. A rate of carbon deposition of higher than about 7 percent of the charge is uneconomic, as the percentage of time "off stream" is too great, or if on-stream time is lengthened the difficulties and cost of burning off this carbon are too great for practicability. The continuous type of process may change this picture somewhat.

Developments up to the present have produced two major types of catalysts, the natural and the synthetic. Natural catalysts include processed clays, bauxite, alumina and silicate materials and other naturally-occurring minerals which receive physical and chemical treatment for purification or improvement of certain properties, but which are still essentially of the same composition as they are in the raw state. Synthetic catalysts include various metallic oxides, such as chromic oxide, tungsten, vanadium and other metallic oxides and ores. These catalysts vary considerably in their efficacy when applied to different stocks and for obtaining different results. Much of the technology of catalytic cracking and reforming, desulfurization, alkylation, polymerization, etc., is developed around the choice of catalyst and operating conditions to fit the material being treated and the product desired. Some catalysts serve for hydrogenation or dehydrogenation, depending on the temperatures, pressures, flow rates and other conditions chosen.

The physical condition of the catalyst also affects importantly the results obtained. In fact the science and technology of catalysis in petroleum refining is so complicated at present that it is next to impossible to induce the informed technologist to generalize on the subject. Consequently, we shall avoid generalization unless qualified by specific data or unless supported by information which appears to be reasonably complete.

It is not desirable to attempt to discuss the char-

acteristics of different catalysts at length here. Variation is too great, and unless the discussion is quite exhaustive the wrong impression may be given. In general, our impression is that the synthetic catalyst is the more efficient per unit of material used, either in speed of reaction produced, or in acccomplishing the desired result under milder operating conditions. The natural catalyst is usually considerably cheaper in first cost, generally more rugged and simple in its preparation.

Yields as reported vary from 30-45 percent of the charge, on a once-through basis in cracking heavier oils, to 95-98 percent when reforming naphthas and the heavy fractions of straight-run gasolines. When cracking heavy oils one of the products is a lighter fraction in the gas oil range, which may either be recycled to the catalyst unit, or is said to be an excellent charge stock for thermal cracking processes. It is because of this fact that catalytic methods are usually studied in connection with thermal-cracking processes. Some technologists are of the opinion that eventually these two methods will go hand-in-hand, each a corollary to the other, and that the efficient refinery of tomorrow will use both if it is to survive.

CRITICAL FACTORS

From the viewpoint of economics the practicability of catalysis in cracking hinges on a half-dozen critical factors, the sum total of which must answer our original question in the affirmative if the refiner is to adopt these methods with a fair chance of realizing a profit from his operations. Other and smaller factors enter into the equation, but these six appear to govern the refiner's decision, in the last analysis.

It has been definitely established beyond the shadow of a doubt that the catalytically-cracked motor fuel, whether from heavy oils, or by reforming (dehydrogenating) straight-run naphthas, is superior in anti-knock quality, and may be made equal or superior to thermally-cracked gasoline in volatility. Also the purity of the catalytic product is considered superior, especially in the reduction of sulfur by catalysts which are employed in conjunction with cracking for sulfur removal. Some more recent developments in thermal cracking which have not been reported on are rumored to improve the status of thermal operations, and the above statements are made without detailed knowledge of the results obtained from these new processes, which may or may not change the correctness of these conclusions.

Therefore, it may be assumed as an axiom that, if catalytic products can carry any extra cost load by virtue of this superiority of qualities the refiner can realize equivalent or greater returns by the adoption of catalytic methods. To the question of whether or not the cost of catalytic cracking is appreciably greater than that of thermal processes we cannot give a definite and unqualified answer. Too little is known as yet of the magnitude of certain factors in cost, especially the details of maintenance of equipment, of equipment life and the frequency of replacement necessary for us to make unqualified statements on the value of this factor. In specific instances indications have been obtained from two years and more of operation of commercial units such as the Houdry units built about 1937. In keeping with the purpose of my paper, I therefore ask this question, with the hope that it will be answered here in such manner as to give the refiner better and much-needed light on this factor: What is the magnitude of the maintenance and replacement costs for a catalytic cracking unit, as compared to those of conventional thermal processes?

One factor which appears in favor of the catalytic process is the less severe operating conditions typical of most if not all these methods. Temperatures are lower or are equivalent to those employed for thermal cracking. Temperature values noted from a recently published article (National Petroleum News, Aug. 23, 1939), on the Houdry unit at Magnolia Petroleum Company's Beaumont, Texas, refinery, show about 900°F. or slightly lower as the maximum temperature attained, that being the temperature of the product from the catalyst cases after reaction. Heat of the charge to the catalyst cases is shown as 880°F., leaving the tubular heater. Pressures are much lower, being 70 pounds in the transfer line to the crude flash chamber, 40 pounds in that flash chamber, and 30 pounds in the catalyst cases. These conditions reduce materially the cost of equipment for the catalyst unit, both in the weight of metal required and in the expensiveness of the alloys used. The omnipresent danger, corrosion, is always with us, and may offset the advtanages of lower temperatures and pressures.

Further proof of the lighter-weight metal which may be used in these processes is the type and sizes of tubes used in the Houdry heater. Tubes of up to 7 inches O.D. have 3/8-inch walls, either plain carbon steel or 2 percent chrome-½ percent molybdenum, a less expensive material than the familiar 4-6 Chrome-½ percent molybdenum tube used in most thermal processes. On the other side of the picture, manv of the transfer lines used in this process in the 15,000-barrel unit referred to are much larger than any used in thermal cracking, lines as large as 24 inches being required to handle the molten salt used as a cooling medium in the catalyst cases.

HEATING COSTS

For a given charge capacity the thermal combination unit requires two heaters, or a combination large heater, one unit for topping the crude, and a second for heating the different fractions to cracking temperature. In some cases, a third heater may be used. The catalytic unit uses only one heater, as for example the Houdry plant referred to, in conjunction with a much greater amount of heat-exchange surface, which is given as 80 percent greater than that in thermal processes of the same capacity. The cost for heating capacity for the catalytic unit has therefore been estimated by disinterested engineers as about half that for the thermal process. Fractionating capacities in the tyo types of process are of the same order of magnitude with any difference probably in favor of the catalytic unit.

To offset any advantage the catalytic process has in the items just mentioned, are the extra items which are not found in the thermal unit. These are the catalyst cases, the catalyst itself, the salt-cooling medium (in the Houdry process), the additional pumps required for handling the larger volumes of liquid, the gas turbines and steam generating equipment used to utilize the excess heat produced during regeneration of the catalyst, and the extra control equipment required for this peculiar on-stream—clean-out—regeneration cycle employed. These extra items for the 15,000-barrel plant at Beaumont include 28 motor-operated valves and the cycle timer which

actuates 23 of them. Eleven salt pumps are used to handle the cooling medium, a turbine-driven compressor of a distinctly new type supplies regenerating air for the catalyst, and a steam generator is added in which the heating medium is the salt used to cool the catalyst. It must be noted carefully in passing, however, that the steam equipment cannot be considered as an additional cost without recompense, since steam so generated is returned to the plant for power or processing, and thus reduces correspondingly the steam which would otherwise be raised by other plant generating capacity. In fact, it is stated that 10,000 pounds of low-pressure steam is returned to the refinery, a credit item which must not be overlooked. The power requirements of the catalytic unit are no greater than those for a similar thermal unit, because of the low pressures employed.

Thirty percent more condenser and cooler surface is needed by the catalytic unit referred to here. Only 60 percent of the thermal unit's oil pumping capacity is required, but the total pumping capacity is 4.5 times that of the thermal unit. The cost, however, is by no means 4.5 times that of the conventional unit, either in installation or in operating costs, again because of the low pressures and lower temperatures employed.

COST COMPARISONS

The net result of all these factors is that the catalyst unit appears to cost more than thermal units of the same capacity. Probably I could have saved time by mentioning the cost of the unit reported recently which is stated to cost $2,980,000 for 15,000 barrels daily crude capacity. This shows a per-barrel cost of $199. A modern thermal unit of like capacity can be built, qualified engineers tell us, for $100 per barrel. This is one of the two hurdles which the catatytic unit must negotiate if it is to survive in the technological battle royal.

The second cost hurdle is that of operation of the unit after construction. And here we must ask another question of those who have the most complete information available on this score: What is the average or typical cost of operating a catalytic unit, in comparison to a similar, modern combination thermal-cracking installation?

There appears to be little if any difference in labor costs, with any advantage probably in favor of the thermal unit. Eight operators and two maintenance men per shift are required on the Houdry unit. To accept published figures of uutilities, 416,000 Btu's per barrel of gasoline made are required by a thermal unit, 554,000 Btu's for the catalytic unit. The electrical energy used is practically the same for both units, 4.30 kwh. for the thermal operation, 4.28 kwh. for the catalytic. Steam requirements are definitely in favor of the catalytic unit, which needs only 46 pounds per barrel of gasoline, as compared to 207 pounds for the thermal process. Thus operating costs appear to be approximately equal, so far as these figures indicate them. One estimate received from highly competent sources is that a once-through catatalytic unit operation will cost 10 to 12 cents per barrel; **complete** thermal cracking will show 12 to 14 cents per barrel operating costs.

No definite data regarding maintenance costs are forthcoming at present, so far as we know. Some units have been operated for two years and more. Yet changes in processing and in equipment have been so rapid that estimates of maintenance costs must be hedged about with qualifications and limitations, so much so that generalizations are not practicable. Temperature and pressure values indicate that wear on equipment from these causes may be expected to be less than on a thermal unit. Corrosion and wear of materials in the catalyst cases and in the salt-circulating system may or may not be excessive, and of such magnitude as to raise the maintenance costs considerably. Further information is needed by the refiner on this point, before he can draw even tentative conclusions.

One of the first items appearing in the refiner's mind is that of catalyst cost, since this is the primary new item in cracking. Mr. Van Voorhis, who did such an excellent job of reporting the details of the Magnolia Petroleum Company unit, tells us that the initial cost of the catalyst there was $18,000. If we assume a permissible catalyst cost per gallon of gasoline of 1/8-cent, and if this unit produces 33.3 percent gasoline, or 5000 barrels per day, it will require 70 days to pay for the catalyst. If the catalyst may be regenerated to operate efficiently during that length of time, the refiner may find it practicable on this item to utilize the catalytic process. Since the unit referred to has operated for 138 days, presumably on the same catalyst charge, and is stated to have been shut down purely for routine inspection after its initial run, the factor of 1/8-cent per gallon of gasoline produced is doubtless too high. Also, it is understood that these catalyst cases are welded throughout and thus closed against simple and easy replacement of catalyst, indicating that a very long catalyst life is expected.

Yields of catalytic gasoline reported vary widely, but an average appears to be between 40 and 45 percent of the charge to the cases. In addition a gas/oil fraction is produced which is said to be first-class charge for thermal cracking, an item which must be considered in the refiner's balance sheet, but which cannot be evaluated here with the required exactness. The Magnolia unit was built, according to published statements, to produce a maximum of gas oil, with gasoline as the less important product, hence the lower yield, we may presume.

ANTI-KNOCK RESULTS

This catalytic gasoline is rated at an octane-number blendnig value of 91.4, in raising a 65.1 octane number East Texas gasoline to 73, L-3, with 30 percent of the catalytic product used. Raising the poorer product 8 octane numbers gives a total of 5600 octane numbers added to 1000 gallons of finished fuel by 300 gallons of the catalytic product. Taking as a representative cost of an octane number in this range the price of 0.06 cents by the use of tetraethyl lead, this knock rating improvement saves $3.36 in lead. Therefore the anti-knock value of this high-octane-number product is 1.12 cents per gallon, which we believe may be accepted as its premium value to the refiner for anti-knock improvement. Continuing, the premium value of the gasoline from a 15,000-barrel unit assuming a 45 percent yield of catalytic product, or 4500 barrels per day, is $2116.80.

And that is the margin, disregarding the improved value of the gas oil suitable for thermal-cracking charge, on which the refiner may plan to cover any additional costs of catalytic cracking operations. That is, these figures are correct if our various assumptions are correct. If we have made errors in

TABLE 1

Results from Catalytic Reforming of Straight-Run Naphthas

	1		2		3		4		5		6		7		8		9		10	
	South Texas Straight Run Gasoline		California Straight Run Gasoline*		Gulf Coast Naphtha		Gulf Coast Naphtha		Gulf Coast Naphtha		Mexican Straight Run Gasoline		Rodessa Naphtha		West Texas Naphtha		Mid-Continent Straight Run Gasolines			
																	Medium		Heavy	
	Chg.	Prod.	Chg.	Prod.	Chg.	Prod.	Chg.	Prod.	Chg.	Prod.	Chg.	Prod.	Chg.	Prod.	Chg.	Prod.	Chg.	Prod.	Chg.	Prod.
Dist. Range	112	88	....	....	314	....	314	....	314	....	106	89	253	125	132	102	122	104	262	110
	408	400	....	....	424	....	424	....	424	....	436	446	394	400	439	466	346	359	438	440
Octane No.	29.1	50.5	51.6	69.3	60.0	70.3	60.0	72.4	60	72.8	39.8	62.0	29.4	50.1	46.4	65.6	45.7	53.8	19.3	43.5
O. N. Increase	....	21.4	....	17.7	....	10.3	....	12.4	....	12.8	....	22.2	....	20.7	....	19.2	....	8.1	....	24.2
TEL Required to 70 O. N. (73-L-3)	3 (66)	1.88	3+	0.50	1.07	None	1.07	None	1.07	None	3.0 (to 61)	1.0	3.0 (to 61.7)	2.0	....	0.63	3+	1.7	....	3.0
Pressure (lbs., gage)	....	30	....	30	....	30	....	55	....	30	....	30	....	30	....	30	....	30	....	30
Temperature ° F	....	990	....	975	....	975	....	975	....	990	....	975 990	....	990	....	975	....	975	....	975
Flow Rate (barrels/ton/day)	....	405	....	400	....	350	....	285	....	350	....	420	....	400	....	391	....	400	....	400
Yield Percent	....	93	....	96.5	....	95.9	....	95.2	....	94.75	....	92.75	....	94.8	....	93.1	....	98.9	....	97.2
V. P. Reid—lbs.	....	....	....	....	1.2	7.35	1.2	8.30	1.2	7.45	....	10.0	0.3	8.95	2.95	10.1	4.3	9.65	0.3	8.85
Sulfur Percent	....	....	....	....	....	....	....	....	....	....	....	Reduced 75%	0.003	....	0.33	0.074	0.048	0.008	....	....

* 33% removed by topping—Bottoms treated and recombined with tops.

assumption or otherwise, a matter which is highly possible, we shall be more pleased than anyone else if the correct data are brought to light.

We will not go into discussion of the various losses in catalytic cracking, losses such as non-condensible or unpolymerizable gases, coke and tar, the last being incorporated in the refinery's heavy fuel oil and having the value accorded to that product in the market. Enough data have been published to give the reading refiner a definite idea of the losses involved, and generalizations here would not likely aid much in further clarifying the situation.

SPECIAL PRODUCTS

From all the information obtainable, it now appears that for the smaller refiner, catalytic reforming and the manufacture of special products by catalytic methods may prove a more immediately attractive field. Officials of organizations developing catalytic cracking of heavier fractions are frank to state that the capacity of the smallest economically practical unit has not been determined, but with the implication that only in the larger units is catalytic operation reasonably certain to prove profitable with the present state of the art. Information which we have been able to obtain and which has not been published indicates that in the fields of reforming low-grade gasoline, alkylation of natural and refinery gases, and desulfurization of high-sulfur products to increase their lead susceptibility and their actual octane rating "as is," catalysis is a tool much needed and very efficient both technically and economically.

CATALYTIC COMPETITION

In these fields also the natural and the synthetic catalysts are competing for first place. The natural catalyst, such as the bauxite product employed by Phillips Petroleum Company, has shown a remarkably long life with maintenance of efficiency which indicates that catalyst cost per unit of product in this type of operation is reduced practically to the vanishing point. Temperatures and more especially pressures are milder than in thermal reforming, are of the order of those referred to earlier as used in catalytic cracking. These conditions reduce costs of equipment and of its maintenance as well as heating costs.

Synthetic catalysts such as chromic oxide and other metallic oxides show a greater initial efficiency than does the natural catalyst, but the cost is much greater. Because of their long life which is claimed to be of the order of 1000 or more possible regenerations, on cycles of up to 24 hours on stream continuously between regenerations, the cost of these catalysts per unit of product is also claimed to approach the infinitesimal. The use of one or the other type of catalyst is determined, we understand, by the specific conditions to be met in any given installation and by variations in properties of the final product which may be desired. In these fields a greater variation in catalyst properties and in operating conditions is made, depending on the nature of the charge. Catalyst and charge are more sensitive to varying conditions than in catalytic cracking. Boiling range of charge bears a closer relationship to the catalyst used and to the temperatures, pressures, and flow rates which give optimum yields and product qualities.

LIFE OF CATALYST

In these reforming operations, which are also of recent application and on which the ultimate in catalyst life has not been definitely determined, the catalysts are operated on as long as 24-hour runs without regeneration. Regeneration is reported to be simple and inexpensive, and the bauxite product, which is inexpensive in the first cost, is said to be slightly better after its first regeneration. As a sample calculation, runs at a rate of 500 barrels per regeneration period per ton of catalyst, continued for 10 runs, the equivalent of 5000 barrels per ton, have shown that the cost assignable to catalyst value is reduced to well under 1 cent per barrel of product formed, a figure considered extremely low. The catalyst at the end of this series of runs showed no appreciable loss of efficiency and can be used, it is understood, for many times this throughput before its efficiency drops to a figure, say 75 percent, which may make its replacement desirable.

Yields of high-octane fuel are 90-97 percent of the charge, as is shown in the accompanying table. The improvement in octane number for these yields varies with the rating of the raw charge, from 8 numbers with a 98.9 percent yield from a Mid-Continent medium heavy naphtha, to 23 numbers on a South Texas straight-run naphtha of 29.1 rating (ASTM) with a 93 percent yield of propane-free product.

The reforming conditions as shown in the table are typified by 975°F. and 30 pounds pressure, with flow rates around 350-450 barrels per ton of bauxite

per day. To single out a few of the results, note the values given for reforming the heavy Gulf Coast naphtha, wherein three sets of conditions were studied, to determine the differences in yield and octane rating of the products. A higher pressure, 55 pounds, and slower flow rate gave a slightly lower yield, 95.2 as compared to 30 pounds and higher flow rate, with appreciable increase in octane number 72.4 as compared to 70.3. The distillation range is vastly improved, changing from 314° F. initial to 102-120°F. with some boost of the endpoint also. This 60-octane naphtha was raised to meet house-brand gasoline requirements without the use of any lead, a saving of 1.07 cc. or about 0.278 cents in cost. Including the 5 percent loss, the refinery price increase for this fuel is 0.54 cents. The vapor pressure was raised from 1.2 pounds Reid to 7.35-8.30 pounds. To observe results on an entirely different type of stock, note also the untreated Mexican straight-run gasoline, containing a large amount of sulfur. Its octane rating was raised from 39.8 to 62.0, an increase of 22.2, equivalent on this stock to a saving of 3.5 cc. of lead, a saving of 0.91 cents per gallon. The yield is 92.75 percent, and only 1 cc. of lead is needed to meet regular-grade gasoline octane rating. Seventy-five percent of the sulfur was removed by this operation, which included 95 percent of the mercaptan sulfur present. Although this sample was almost completely paraffinic, the reformed product contained 22 percent of unsaturated hydrocarbons.

Rodessa naphtha is notoriously low in octane number. The sample of very low sulfur (0.003 percent) shown in the table, was boosted from 29.4 octane number to 50.1, a gain of 20.7 numbers. This product required only 2 cc. of lead to bring it to 70.1 ASTM octane rating, while 3 cc. in the original product raised its rating to only 61.7 ASTM. The yield is 94.8 percent, including the propylene polymers formed in the auxiliary unit from the olefinic gases produced by the reaction.

The data given in this tabulation are selected at random from an exhaustive pile of reports of studies on the most widely varying types of straight-run gasolines and naphthas, to give a fairly comprehensive idea of the results which have been obtained from these operations. Because of the ruggedness and long efficiency life of the catalyst, the low pressures and the normal-for-cracking temperatures, consequently the relative cheapness of the equipment required, the low labor and utilities costs, the relatively very low percentage of time off-stream from regeneration and the high yields, the technologists best acquainted with these operations are convinced that this type of operation for the average-to-small as well as the largest refiner is widely and generally applicable as an assured and economically profitable venture. Such operations are being carried out on a large scale in commercial units and are likely to be applied more extensively in the near future, we understand.

SYNTHETIC CATALYST

The foregoing method of reforming by catalysis may be considered, for purposes of differentiation, as more or less comparable to thermal methods, with the major differences that yields are normally higher and octane number improvement may be higher or lower as the operator may choose. Still other methods, especially one using a synthetic catalyst, is also more or less similar to thermal methods, except that octane numbers of 78-80 are obtained instead of 72-3, with yields comparable to those from thermal reforming processes.

A new method of once-through reforming uses a synthetic catalyst, but by methods which cannot be discussed here, octane numbers above 90 may be obtained, with of course a sacrifice in yield. Several units of this type involving more than 40,000 barrels daily capacity are under design or construction, we are told, and this process also adapts itself to much smaller units than seem feasible for catalytic cracking. From a 100-barrel-per day unit which has been operating for some time in the same refinery where thermal reforming is also carried on, the following comparisons have been obtained:

> By thermal reforming and catalytic polymerization, a 68 percent yield of 84-octane gasoline may be produced.
>
> By this catalytic process a 78 percent yield of 84-octane fuel is produced.
>
> By this catalytic process an 85 percent yield of 80-octane fuel is made.
>
> By the same thermal methods, production of 88-octane fuel gives only a 60 percent yield; a fuel of the same octane number is produced in 76 percent yield.

This catalyst is said to operate on cycles as long as 10 hours; a well-known engineer has remarked that this process, in his opinion, is the "cheapest way to make a lot of octanes." One interesting point about this product is that the heavy end of the fuel is as high in octane number as is the light end. It is highly aromatic, but contains practically no benzol, its acid heat test making it satisfactory to meet aviation-fuel specifications. End points of 437-450° F. are satisfactory, which of course boosts the overa-all yield.

Production costs for this product, we understand, are somewhat higher per barrel of charging capacity than for a thermal-reforming unit of the same size, but the increased yield counterbalances the higher cost. For average conditions, that is producing 74-octane gasoline, the economics of this process is understood to be about the same as that for thermal processes. For producing higher octane numbers the economics gives a much greater advantage to the catalytic method. Therefore if this type of process is as practicable in smaller units as we understand it to be, such a method may become the refiner's best protection against rising octane numbers and the eternal race to "make 'em better." Design calculations and commercial experience with this process have shown that a 3000-barrel unit is a safe proposition economically. A 1000-barrel unit is under design, and experience with that unit will clarify greatly the question of how small a unit is practicable.

DESULFURIZATION

The continuous reforming unit, costing 60 percent as much as the intermittent type, is now considered practicable in almost any size unit; installation of several of these units are assured during the next 12 months or less time.

Still another development which is of major importance to refiners generally is the desulfurization of gasolines and naphthas by catalysts, especially bauxite. Lead susceptibility is inversely proportional to the amount of sulfur present in the naphtha, and high sulfur increases lead costs to a serious, sometimes prohibitive degree. By treating naphthas in the presence of bauxite catalyst at, for example, 15 pounds pressure and 750° F., at a rate of two liquid volumes of charge per volume of catalyst, the major

TABLE 2

Sulfur Removal and Lead Susceptibility with Bauxite Catalyst

	Gasoline Distillate		West Texas Naphtha			
	Charge	Product	Charge	Product	Charge	Product
Total Sulfur Percent	0.425	0.011	.....	.....	0.143	0.005
Octane No. ASTM	44.8	48.1	45.4	49.6	58.5	61.0
Lead, cc/gallon	3 to 56	2.04 to 70	3 to 59.8	3 to 70.5	1.74 to 71 (or 2.25 to 73)	1.0 to 73
Lead response/10-O.N.	2.73	0.91	2.10	1.43	1.20	0.83
Distillation Range	98-392	100-396	137-440	132-445	.....	.....
Vapor Pressure—Lbs. Reid	8.25	9.50	3.05	3.15	.....	.....
Pressure—Lbs.	.....	15	.....	15	.....	15
Temperature °F	.....	750	.....	750	.....	750
Flow Rate/(bbls./ton/day)	.....	255	.....	.....	.....	.....

portion of the sulfur is eliminated, the octane number of the treated gasoline is raised appreciably, and its lead susceptibility is remarkably increased.

In Table 2 are given the conditions of treatment and the results obtained by such a catalytic treatment. The octane number of a straight-run gasoline distillate of 400° F. endpoint is raised from 44.8 to 48.1 ASTM, sulfur is reduced from 0.425 percent to 0.011 percent. One cc of lead raised the octane rating of the charge to 50.1; the same amount raised the rating of the treated product to 63.4. Three cc of lead raised the raw material to only 56, while 2.04 cc raised the treated gasoline to 70, ASTM. Under about the same conditions a West Texas distillate was robbed of sulfur, 0.143 percent to 0.005 percent, while its susceptibility to lead was increased from 6.9 octane numbers per cc added, to 12 octane numbers per cc for the treated product.

This process has also been applied to a large variety of high-sulfur naphthas and gasolines, and the results given are typical, judging from perusal of other results from the treatment of these products.

No generalizations regarding catalytic reforming or desulfurization costs can be made, further than to state that the over-all cost per unit of product of a given degree of improvement is equal to, in most cases, less than that for thermal reforming, and less than the cost of lead required to attain the same octane rating. The actual improvement in octane rating by reforming—or dehydrogenation as it is sometimes called—varies with the rating of the raw material, the lower the original rating the greater the improvement. As a cheap means of improving octane number and volatility at the same time, this type of process with its high yields appears to have a definite place in the refiner's technology.

FOR AVIATION FUEL

Recent developments in the manufacture of extremely high octane number fuels valuable for making the aviation super-fuels so much discussed in recent months are of particular interest to the refiner who may wish to enter this field, either for making these fuels or to produce a very high-blending-value material for regular or premium gasoline improvement. In a four-step process recently placed on a commercial basis by Phillips Petroleum Company several catalytic steps are involved in effecting the dehydrogenation to olefins, polymerization, hydrogenation of the polymer, and catalytic cracking of the overpolymerized heavy products to reduce them again to the desired boiling range. This four-part process yields isooctane and its homologues, of 95-octane number or higher, too low in vapor pressure to serve as aviation fuel alone, but when combined with isopentane and other high volatility, high-octane number products, gives a fuel which is superior to any known today for the most exacting aviation purposes.

ALKYLATION

These same or similar catalysts are also used to accomplish the alkylation of isoparaffins such as i-butane. In this process the selected fraction of natural or light refinery gasoline is divided, and no preliminary treatment is given the fraction containing essentially pure i-butane. The other fraction which may be either butane or other hydrocarbons, is cracked to yield the optimum amount of olefins, which are then reacted with the uncracked i-butane to yield isoparaffins of 95-100-octane number. The purity of the final product depends on the degree of purification of the raw materials. These reactions may be accomplished either by thermal or catalytic methods, and the thermal process is now being used to produce some interesting and invaluable new fuels, of especially great interest to us now, in view of the developments in both military and commercial aviation.

The manufacture of neo-hexane, or 2.27-dimethyl butane is on a commercial basis and facilities will be extended in a short time to produce several hundred barrels per day of this almost mythical fuel. With an octane rating of nearly 100 (95-96) as it comes from the plant, neo-hexane has 9.5 pounds Reid vapor pressure. It therefore need not be blended with lower vapor pressure material to obtain the needed volatility, having both vapor pressure and octane rating in its own right. If desired it can be blended with isopentane, and with iso-octane to give a typical distillation curve. This product is considered now as the best source of the 115-octane number fuel about which our aviation fuel and engine technologists are thinking so longingly.

Neo-hexane is produced by thermal methods. Isobutane is concentrated from mixed gases, and essentially ethane is concentrated in another fraction. This lighter fraction is cracked by heat and pressure to produce mainly ethylene, which is then reacted with the i-butane, and the six-carbon alkylation product is purified by distillation to yield the finished fuel in whatever degree of purity is desired. Concentration by distillation is the most expansive step in the process, with the cracking of ethane as the next most costly. The finished product, we understand, can compete with other super-fuels satisfactorily in price, and the amount which can be economically produced is limited only by the demand for such a fuel.

New Developments in Burners and Their Application*

E. L. DENNIS
Coppus Engineering Corporation

PRELIMINARY to discussion of new developments and applications in gas burners, discussion of the theories of combustion of hydrocarbons together with the mechanism of heat transmission should be presented. This, naturally, involves the furnaces and heat absorbing elements combined in the furnace in which combustion takes place.

Combustion is a series of chemical reactions of progressive oxidation of a combustible material. These reactions liberate heat in amounts proportionate to the degree of oxidation carried out, the chemical analysis of the fuel, and the rate of fuel consumption. If sufficient oxygen is supplied to complete the chemical reactions, the same amount of heat will be produced regardless of the rate of combustion or intermediate steps that may or may not exist during the process of complete combustion. This does not mean that the recovery of the heat produced will be the same in all cases. The speed of combustion of a hydrocarbon is governed by several factors, chief among these being the intimacy of mixture of the combustible and oxygen molecules in the air supplied for supporting the combustion and the speed of mixing of the air and the gas streams within the furnace where premixing is not employed. The temperature of the combustion chamber also has a positive catalytic action on the speed of combustion.

The chemistry of combustion of a hydrocarbon is generally shown in a chemical equation where complete oxidation is indicated and stable end products are produced. Thus, the chemical reaction of methane, the most simple of the hydrocarbon gases, is generally shown as:

$$CH_4 + 2O_2 = CO_2 + 2H_2O \qquad (1)$$

It is generally conceded that the molal heats of the above reaction relating to combustion will liberate 383,771 B.t.u.'s.

Taking this reaction as typical of the reaction of all hydrocarbons in combustion, let us analyze actuallly what it means. First, no matter is gained or lost in any reaction. "Matter cannot be created or destroyed." Second, the total energy of the reaction, that is, amount of B.t.u.'s produced, is the same regardless of the intermediate reaction that might take place to govern the speed of the reaction. "Energy cannot be created or destroyed."

However, on analysis of Equation 1, it is only necessary to note the combustion end products, viz.; CO_2 and H_2O, to realize that somewhere in the reaction of oxidation or combustion some of the hydrogen atoms have become separated from the carbon atoms, because water vapor is only formed by the burning or oxidation of the hydrogen atoms, or released as water vapor in the chemistry of formation of a new product. It is also apparent that the carbon atom must undergo some chemical changes in order to oxidize direct to CO_2.

INTERMEDIATE REACTION

It is stated by a number of authorities on the chemistry of combustion, that there is intermediate reaction of hydrocarbons in combustion, in which alcohols, aldehydes, and acids may be formed during the process of oxidation, but on account of the very unstable conditions of the intermediate products that could be produced during the process of combustion and the high temperatures involved, we have been unable to find any authority that can actually state exactly what intermediate products are formed and in what proportions, that would take place at normal temperatures of furnace combustion.

It is not the purpose of this paper to delve too deeply into the actual chemical reactions of combustion, but the purpose of bringing out the deductions, is to call attention to the weaknesses of Equation 1. We do not have means, as previously stated, of actual determination of the intermediate reactions that have to occur before water vapor and carbon dioxide can be formed. It is our contention that the reaction is variable and to some extent governable by the temperatures of the furnace, design of the furnace, and design of the burner employed. We do contend that the aldehyde must occur before combustion is completed.

Thus, a burner may be designed to retard the speed of reaction of combustion, giving a long lazy flame and requiring more furnace volume in which to complete the reaction. Likewise, a burner may be designed to increase the propagation of flame or the speed of reaction and require far less furnace volume in which to secure complete combustion.

For example of intermediate reaction that could take place before Equation 1 is completed to the end products, we give the following possible oxidations in progressive steps which could take place in laboratory practice. We wish to cite at this point that it

* Before the Manuwacturers' Commitee, Western Petroleum Refiners Association, Wichita, Kansas, October 5, 1939.

must be specifically understood that the reactions brought forward are simply chemical possibilities and not intended to give the direct formula of combustion, as otherwise a storm of protest by those more versed in the art of chemistry of combustion might be brought down on our heads. It has been proven, though, that some, if not all, of the intermediate products shown in the following reaction, have been isolated from the combustion gases of methane and therefore it should be conceded that some of the reactions of combustion might well follow the general organic reaction of oxidation of hydrocarbons. Repeating Formula 1

$$CH_4 + 2O_2 = CO_2 + 2H_2O \quad (1)$$

The first reaction of the hydrocarbons might well be oxidation as shown by the following:

$$2CH_4 + O_2 = \underset{\text{(Alcohol)}}{2CH_3OH} \quad (2)$$

The next reaction by hydroxylization

$$2CH_3OH + O_2 = \underset{\text{(aldehyde)}}{2CHOH} + \underset{\text{(end product)}}{2H_2O} \quad (3)$$

By next step of oxidation

$$\underset{\text{(aldehyde)}}{2CHOH} + O_2 = \underset{\text{(acid)}}{2CHOOH} \quad (4)$$

Next step by dissociation of the acid

$$\underset{\text{(acid)}}{2CHOOH} + \text{Heat} = \underset{\text{(end product)}}{2H_2 + 2CO_2} + \text{Heat} \quad (5)$$

The last reaction by oxidation might be

$$2H_2 + O_2 = \underset{\text{(end product)}}{2H_2O} \quad (6)$$

Summarizing Equations 2, 3, 4, 5 and 6

$$\underset{(2)}{2CH_4} + \underset{(2)}{O_2} + \underset{(3)}{O_2} + \underset{(4)}{O_2} + \underset{(6)}{O_2} = \underset{(5)}{2CO_2} + \underset{(3)}{2H_2O} + \underset{(6)}{2H_2O}$$

By condensing the above reaction we find

$$2CH_4 + 4O_2 = 2CO_2 + 4H_2O$$

By reducing the mols entering into the reaction shown above, we secure

$$CH_4 + 2O_2 = CO_2 + 2H_2O$$

which will be recognized as Equation 1, the accepted formula of the complete reaction of methane with oxygen in combustion and the corresponding end products are carbon dioxide and water.

INFLUENCING FACTORS

There are a number of influencing factors that may change the reaction of the intermediate products cited, which would prevent the positive and progressive oxidation as shown. We recognize also that methane could possibly form a different alcohol from the methyl alcohol shown in the first reaction of oxidation. We are not sure that the hydrocarbon CH_4 might not combine with the two mols of oxygen and four mols of methane, forming a higher alcohol than the one cited, which would be ethyl alcohol, or C_2H_5OH. However, in either event it is possible that the reaction could be completed continuously through the alcohol stage forming the aldehyde only, which could be dissociated by liberation of hydrogen. But in either event it is a relatively easy matter to break down the reaction of methane to the final end products shown in the examples cited above. Any dissociation of intermediate products of combustion due to temperatures in which they are present would tend to destroy the balanced equations indicated, but nevertheless it is these factors that we wish to bring out as possibilities and which would be to a great extent dependent on furnace conditions and the functions of the burner. Recognition that the aldehyde of any hydrocarbon must be present in the products of combustion before hydrogen is released has been indicated by a number of authorities and reference to this can can found in the handbooks of the American Gas Association, and also Kent's Volume II on Power, pages 4-48. The presence of aldehyde can be established to the satisfaction of the laymen by physical observations with any gas fired furnace. None who has had material experience with gas fired furnaces has failed to observe that when insufficient air is admitted for complete combustion a characteristic pungent odor will be distinctly noticed. We have often heard it referred to by firemen, by their remark, "I smell CO." This statement comes from their knowledge that when this odor is present the flue gas samples invariably show the presence of CO, which is well known to be an odorless gas. This odor is the characteristic odor of an aldehyde and any high school chemist recognizes that the odor of the aldehydes is one of their characteristics which is unfailing in identification. Granting this fact as true on the face of positive identification of the aldehyde when insufficient oxygen is supplied to complete the reaction of Equation 1, it is clearly indicated that at least part of the reaction of combustion was forced to stop in the intermediate reaction shown in Equation 3. We also know that if the air supplied is further reduced beyond the first indications of aldehyde determined by odor, that smoke will begin to appear in the products of combustion. This clearly indicates that cracking action on the hydrocarbon and actual liberation of free carbon is occurring. We bring this out to show the controllability of combustion and believe that it is worthy of considerable research to determine definitely just what the chemical reactions of combustion are under various conditions, and also the possibility of investigation of catalysts that might be employed to govern the reactions.

PRIMARY AND SECONDARY COMBUSTION:

When all of the air for combustion is delivered into a furnace thoroughly mixed with the hydrocarbon gas, primary combustion only, will occur. Such combustion conditions can be secured by the premixing type of burners. When additional air is admitted that does not mix with the gas until combustion is partially completed, secondary or delayed combustion will take place. Secondary air may be admitted in separate openings other than the burner but also may be admitted through the burner proper, unless positive means of preventing stratification of the air stream and get jets are provided. In burners not of the positive mixing types, some secondary air has to enter the furnace and result in secondary combustion.

We can picture the reaction difference when secondary combustion has to occur by admission of secondary air as requiring additional reactions in oxidation of the aldehyde in four steps when it is possible to conceive that with primary combustion alone the aldehyde will break down into CO_2 and H_2 in one step, which indicates the speed of combustion will be more rapid with primary combustion only

as compared to both primary and secondary combustion.

Let us assume that in the first and second hydroxylization reactions two mols of acetyaldehyde are formed which would have the formula 2 CH_3CHO.

If the oxygen molecules were not present in sufficient quantity in the zone of primary combustion the following might well be the chemical reaction:

$$\underset{\text{(aldehyde)}}{2CH_3CHO} + O_2 = \underset{\text{(acid)}}{CH_3COOH} \qquad (1)$$

Then additional oxygen in secondary air will come in contact with the acid and oxidation of secondary combustion take place as:

$$2CH_3COOH + O_2 = 4H_2 + \underset{\text{(end product)}}{(2CO_2)} + 2CO \qquad (2)$$

Further oxidation of the CO and H_2 liberated would follow as:

$$2CO + O_2 = \underset{\text{(end product)}}{(2CO_2)} \qquad (3)$$

and

$$4H_2 + 2O_2 = (4H_2O) \qquad (4)$$

Summarizing the reaction of the aldehyde:

$$\underset{(1)}{2CH_3CHO} + \underset{(1)}{O_2} + \underset{(2)}{O_2} + \underset{(3)}{O_2} + \underset{(4)}{2O_2} = \underset{(2)}{2CO_2} + \underset{(3)}{2CO_2} + \underset{(4)}{4H_2O}$$

Condensing to:

$$2CH_3CHO + 5O_2 = 4O_2 + 4H_2O \qquad (5)$$

It is perfectly logical to assume that if all of the combustion is primary, the aldehyde, being unstable in nature, will break down in one reaction and thus eliminate the acid radical from every occurring and in which case the reaction of the aldehyde to end products would be simplified to:

$$2CH_3CHO + 3O_2 = \underset{\text{(end product)}}{4CO_2 + 4H_2} \qquad (1)$$

and

$$4H_2 + 2O_2 = \underset{\text{(end product)}}{(4H_2O)} \qquad (2)$$

Reducing the number of oxidation reactions in primary combustion to two as compared with four where secondary combustion is present and resulting in the same end products as by summarizing:

$$\underset{(1)}{2CH_3CHO} + \underset{(1)}{3O_2} + \underset{(2)}{2O_2} = \underset{(1)}{4CO_2} + \underset{(2)}{4H_2O}$$

Condensing to:

$$2CH_3CHO + 5O_2 = 4CO_2 + 4H_2O$$

which is the same general reaction indicated in (5).

In each case the total heat liberated will be the same but the speed of the reaction with primary combustion alone will certainly be increased. Complete oxidation or partial oxidation of the hydrocarbon aldehyde is acknowledged by several authorities.

MECHANISMS OF HEAT PROPAGATION AND TRANSMISSION:

Referring to the hydrocarbon gases, these may be classed as producing a non-luminous flame in radiant furnaces with sufficient oxygen present for complete combustion. Unless the flames are non-luminous such large furnace volumes would be required that the heat input possible per cubic foot furnace volume per unit of time would be so small that the general requirements of industry would not be met.

The products of combustion during flame propagation being gases, will, under the same pressure conditions, occupy or fill a space in direct proportion to the quantity of gas being consumed and the absolute temperatures. As furnace pressures are so nearly constant the factor of gas volume in relation to pressure may be disregarded. "The volume a gas assumes is in direct proportion to the absolute temperature and inversely proportionate to the absolute pressure."

Therefore, when the reaction of combustion of a gas is speeded up, the temperature of the combustion gases will rise as all of the heat is liberated nearer the burner and the combustion gases will expand closer to the burner tending by expansion due to temperature to spread over the furnace nearer to the front or burner wall, but the heat distribution can be governed. With increased combustion speeds, it will be seen that much higher heat releases can be secured in a furnace than is possible where secondary combustion takes place.

From this point we must go into the mechanisms of heat transmissions.

We can consider that by propagation of combustion from gases, accepted as producing non-luminous flames, a mass of heated gas is liberated into the furnace containing a certain amount of thermal heat and having a temperature proportionate to the rate of combustion and somewhat inversely proportionate to the mass occupied. Therefore, the temperature of combustion will be higher with less excess air, provided combustion is complete to the end products because of less mass and higher again if combustion is completed in less volume of the furnace.

Transmissions of heat is accomplished by only three mechanisms, conduction, convection, and radiation. Usually when transmission of heat takes place all three of the mechanisms are employed to some degree and the quantities transferred in furnace designs can be controlled to some degree into each of the thre mechanisms. Furnace design, location and distribution of the heat absorbing surfaces of a furnace are prime factors in governing the heat transmission efficiency of a furnace.

In speaking of the efficiency of a furnace we refer to the amount of heat absorbed by the surfaces, such as tubes, and transmitting this to other fluids, etc., separated from the combustion gases of the furnace by the retaining walls, in proportion to the amount of heat liberated by the combustion in the furnace. The mechanism of absorption of heat through the material of the retaining wall of the fluid will naturally be more by conduction than either by convection or radiation.

In turn, the temperature of the retaining walls, or amount of transmission of heat to the walls, will be more by radiation and convection than by conduction.

The definitions of the three mechanisms of heat transmission are:

Conduction: Transfer of heat from one part of a body to another part of the same body, or from one body to another in physical contact with it, without appreciable displacement of the particles of the body.

Convection: Transfer of heat from one point within a fluid, gas, or liquid, by mixing of one portion of the fluid with another of different temperature. In natural convection, that is, without forced mixing from external source, the motion of the fluid is entirely the result of density resulting from temperature differences within the fluid mass.

Radiation: Transfer of heat from one body to another, not in contact with it, by means of wave motion, of heat rays, through space.

The physical laws governing transmission of heat

by three mechanisms are available in any mechanical or chemical engineer's handbook. We use these in the following development of the furnace mechanism without specific quantitative analyses.

When a furnace is operating under normal conditions a condition of stability of heat transmission from the heat liberated in the combustion products to the heat absorbed by the surfaces supplied for that purpose will be essentially established. Conduction, convection, and radiation factors will be established in relatively the same proportions of the total amount of heat transferred.

McAdams, in Heat Transmission, states, in the chapter on Radiant Heat:

"Of the gases encountered in heat-transfer equipment, carbon monoxide, the hydrocarbons, water vapor, carbon dioxide, sulphur dioxide, ammonia, and hydrogen are the only ones with emission bands of sufficient magnitude to merit consideration."

In the combustion of the saturated hydrocarbons, McAdams further states, under the heading, Radiation from Non-Luminous Gas Flames and Flue Gas:

"The constituents, carbon dioxide and water vapor, account for the major portion of the radiation of gases in furnace chambers, and no large error is introduced by neglecting the others."

"The amount of heat radiated by any particle is proportionate to the fourth power of the absolute temperature." (This is established in the "Stefan-Blotzmann Law"—$q = 0.172\ p\ A(T/100)^4$ where A= radiating area, p = the emissivity factor of the surface and T = absolute temperature in degrees F.)

Gases containing carbon dioxide and water vapor when heated to high temperatures emit invisible infrared rays of radiation. (Mark's Handbook, Third Edition, page 409): *"Under conditions of high temperature and thick gas layer or high concentration of the radiating constituents, water vapor and carbon dioxide, this mechanism (Radiation) of heat transfer from gases to surfaces outweighs that of Convection in importance."* (See Industrial and Engineering Chemistry, Volume 19, page 888 for calculations of this type.)

In radiant heat transfer from one solid to another several laws come into effect.

One being the emissive power of the surfaces, which is established for most materials, and is equal

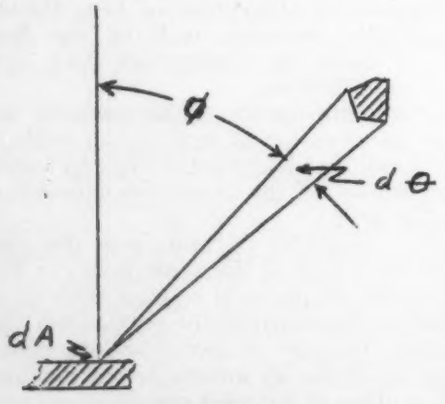


FIGURE 1

to the total radiant energy radiated in all directions from the surface of one side per unit of time per unit of area or B.t.u. per hour per square feet.

The intensity of radiation from a surface, designated by, i. in Figure 1, is the radiant energy emitted per unit of time, per unit of solid angle with the apex at the radiating area, per unit of projected radiating area, the projection being onto a plane normal to the radiating beam. Let dA (Figure 1) equal a small surface element of a radiating body. Within the solid angle, $d\Theta$, making an angle ϕ with the normal to dA, let the quantity of energy being emitted from dA per unit time equal dq. Then the intensity, i, of radiation of the surface dA in the direction of ϕ is defined by the equation

$$dq = i\ dA\ d\Theta \cos \phi$$

The normal intensity of radiation is that value for i when the angle ϕ is zero.

The absorptivity of radiant energy of a surface is that fraction of radiant energy, incident on the surface which is absorbed.

The reflectivity of a surface is that fraction of radiant energy, incident on the surface, which is reflected.

The transmissivity of a substance is the fraction of radiant energy incident on it which is transmitted through it by radiation.

It will be seen that since energy cannot be created nor lost, that the sum of the absorptivity, reflectivity and transmissivity will equal unity. However, for thick opaque bodies or solids the transmissivity equals zero and then the sum of absorptivity and reflectivity will equal unity.

FURNACES AND BURNERS:

The function of the furnace is to serve as the vessel for combustion and as a means of transmitting heat to the surfaces employed for transmission of heat to other bodies by absorption of part of the heat generated by the combustion. In boilers, stills, and heaters, tubes are employed for conducting fluids through regions heated by the furnace gases directly or indirectly. All tubes that are placed so they can "see the fire" or subject to radiant heat from the furnace walls and floor are generally classed as "radiant tubes," and the rest of the tubes are classed as "convection tubes." This is because they absorb generally speaking, most of their heat by the mechanisms of radiant heat and convection respectively, however, as a matter of fact, both absorb heat by both mechanisms, and also by conductivity.

The burner delivers into the furnace highly heated gases that give up heat as follows:

By radiation to the walls and floors where it is reradiated to the tubes visible to the walls and floor.

By radiation from the furnace gases due to the radiant properties of water vapor and carbon dioxide present at high temperatures direct to the tubes classed as radiant tubes.

By convection to the radiant tubes due to mixing of the hotter gases in the combustion zone with the gases cooled by the radiant tubes.

By conductivity within the furunace gases and through the "film" of cool gases naturally surrounding the radiant tubes. (The so-called gas film surrounding a tube in an incandescent furnace has no bearing on the amount of radiant heat absorbed as the rays of radiant heat penetrate this film unreduced.)

The balance of the total heat in the combustion gases will enter the "convection" tubes with the exception of the loss due to radiation from the furnace walls. Therefore, the more heat absorbed by the radiant tubes, the less absorption will be done by the convection tubes as the gases will enter the convection sections at lower temperatures and volumes

Recessed Versus Exposed Tubes in Radiant Furnaces

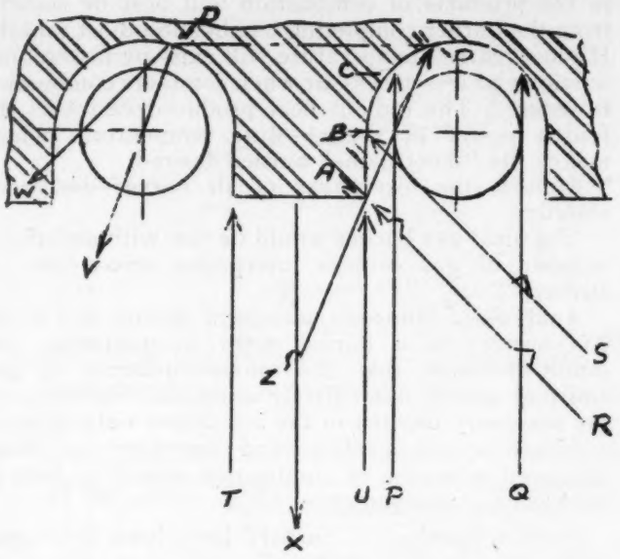


FIGURE 2

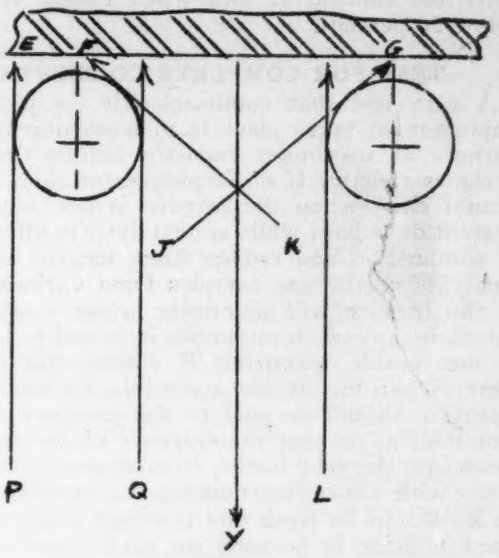


FIGURE 3

Figure 2 and Figure 3 are shown for comparison purposes. Figure 2 represents two radiant tubes recessed in the refractory while Figure 3 represents identical tubes exposed, or in front of the refractory. Before comparison it must be stated that when fuels of extreme combustion temperatures, such as powdered coal or refinery coke, are employed, the tubes should be installed as in Figure 3 as they serve as a screen to the refractory walls and prevent burning. However in gas, or combination gas and oil fired furnaces, very often the arrangement as shown in Figure 2 is of great advantage and always on gas fired furnaces only.

In Figure 2, lines T, Z, U, P, Q, R and S represent emission bands of radiant heat to the refractory surface. In Figure 3, lines Q, L, J and K represent similar bands. Heat absorbed by the wall tubes from the refractory shown is only by re-radiated or reflected heat. In both cases, the area between lines P and Q include the fire side of the semicircular area of the tube. These will absorb the same amount of heat from combustion gases of the same temperature and re-radiated heat from walls and floors of equal area and temperature. In Figure 2, it will be noted that the normal angle of re-radiation from the curved surface will radiate more heat to the rear half of the tube, as indicated by lines V and W. The area between lines T and U, Figure 2, re-radiates no heat to the recessed tubes and reaches a temperature several hundred degrees higher than any surface of the refractory shown in Figure 3. Therefore, the intensity and amount of re-radiated heat from the refractory in Figure 2, line X, is much greater than from the refractory in Figure 3, line Y. This intensified re-radiation from Figure 2, Section TU, increased radiant heat re-radiation to any other tubes included in the furnace in "sight" of the areas encompassed by TU. The catalytic action due to this area speeds up combustion and increases temperature of combustion which in turn increases the intensity of the radiant heat emanating from the products of combustion.

for the same heat release rates. The convection section becomes more efficient however as on account of reduced velocity due to reduced temperature the gases in the convection section will give up more heat by longer period of contact.

The convection section of the furnace absorbs heat from the gases chiefly by the mechanism of convection as the name implies, but considerable amount of heat is absorbed by radiation from the carbon dioxide and water vapor present.

The efficiency of the tubes, as heat absorbers, should be given serious consideration. Thickness of wall should be maintained as thin as practical and tube surfaces should not only be as near the theoretical "black surface" which absorbs without reflecting heat, but should also avoid smooth finish. Of course, alloy tubes are necessary where corrosion exists either on the interior or exterior surfaces. Pressures generally should determine wall thickness.

A "reducing" atmosphere will exist in a furnace when combustion is incomplete and this results in serious impingement on the tube areas either locally or generally. Secondary combustion as previously explained will create this condition when heat releases per cubic foot per hour exceed the burner capacity for complete combustion before impingement on tubes or walls.

High furnace temperatures sometimes make secondary combustion invisible to the eye, however, when typical tube failures occur or failures in tube sections located where the combustion gases enter the tube banks is observed, this can usually be suspected to be due to secondary combustion at these locations creating local "hot spots" due to hydrogen liberation taking place. A reducing atmosphere is more damaging to tubes than oxidation.

An "oxidizing" atmosphere will exist in a furnace where excess oxygen is present at the termination of the combustion zone. The very high temperatures existent at the fringe of secondary combustion is an ideal medium for oxidation of metals. Therefore, it is logical to assume that when secondary combustion occurs at or near tube surfaces, not only are the tubes subject to reduction action but also to oxidation. This combination of reducing atmosphere followed by an oxidation atmosphere within or near tube areas and taking place in distances that may well be less than an inch in dimension, is extremely dangerous and greatly reduces the normal life of tubes visible to the furnace.

Direct flame impingement is to be avoided.

A "neutral" atmosphere exists in a furnace pro-

vided combustion is complete within the furnace without impingement and the inert gases CO_2 and H_2O vapor, and nitrogen only, exist when the gases enter the tube areas and when excess air is kept below 10 percent.

TEST FOR COMPLETE COMBUSTION

A sure test that combustion is complete before impingement takes place is to momentarily fire the burners at maximum capacity before the furnace becomes radiant. If no impingement then occurs, it cannot exist when the furnace is hot, since incandescent or radiant walls are catalytic in effect on rate of combustion and reduce flame lengths materially. Analyses of the gas samples from various sections of the furnace will determine when combustion is complete, as carbon monoxide is bound to be present in measurable quantities if combustion is incomplete. When means are accessible for testing, more attention should be paid to the presence of carbon monoxide at or near the entrance of the combustion gases into the tube banks. In analyses of combustion gases with Orsat instruments, the chemicals should be known to be fresh and readings made until constant volume is secured on each constituent gas, otherwise errors may occur. A standard procedure for flue gas analyses should be followed.

BURNER IMPROVEMENTS:

The definite trend in recent years in design of burners has been towards a "short flame" type with means to secure this. The long prelude establishes that furnace conditions in capacity of B.t.u. input per hour, increased radiation from the walls and floors as well as from the presence of CO_2 and water vapor in the products of combustion will best be secured from the burner completing combustion most rapidly. Higher "flame" temperature will exist by faster combustion and less excess air when complete combustion is secured. The radiant heat produced varies as the fourth power of the absolute temperature which makes the "short flame" burner desired.

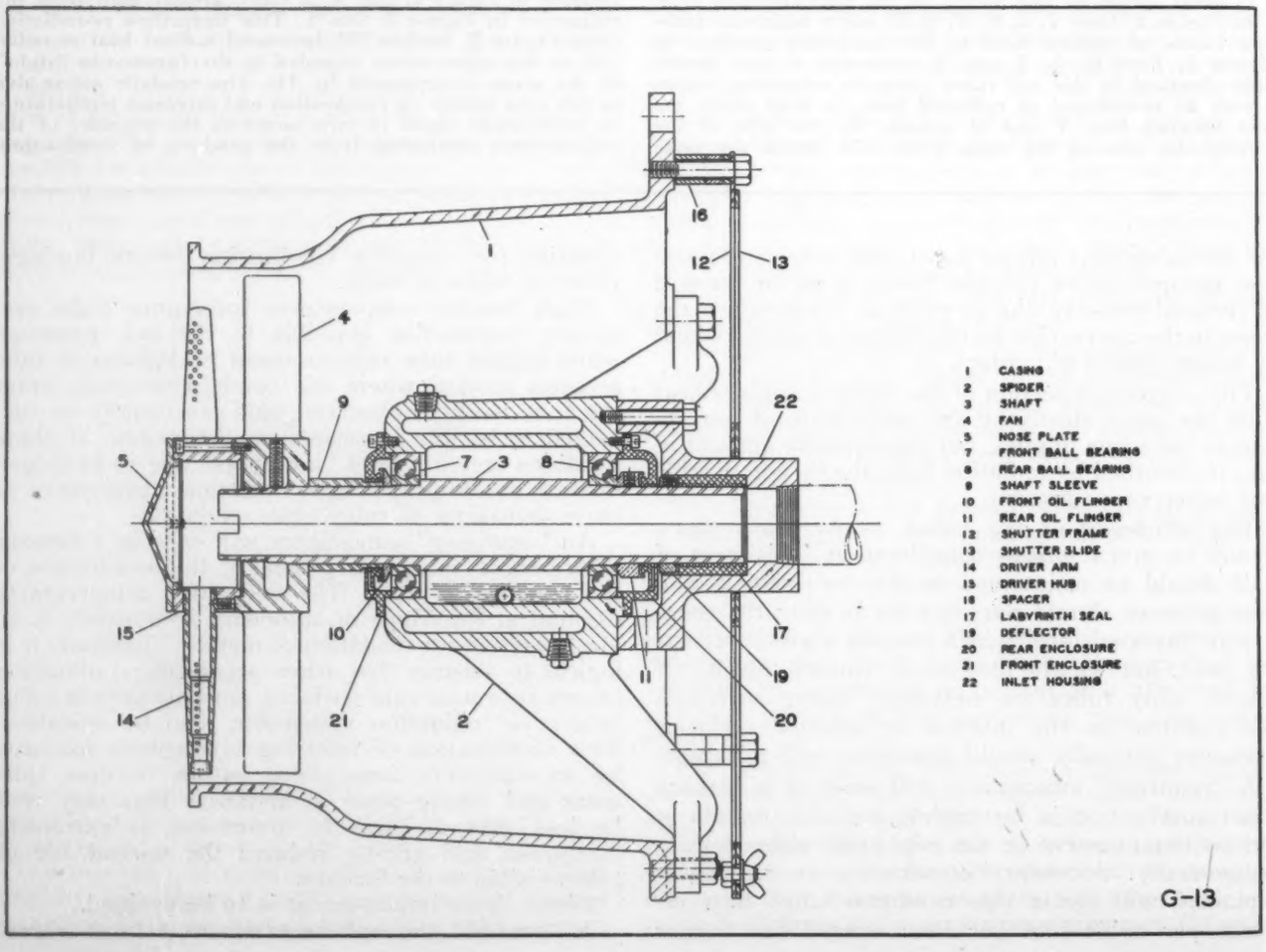
Bunsen, the forerunner of all burner designers, stated:

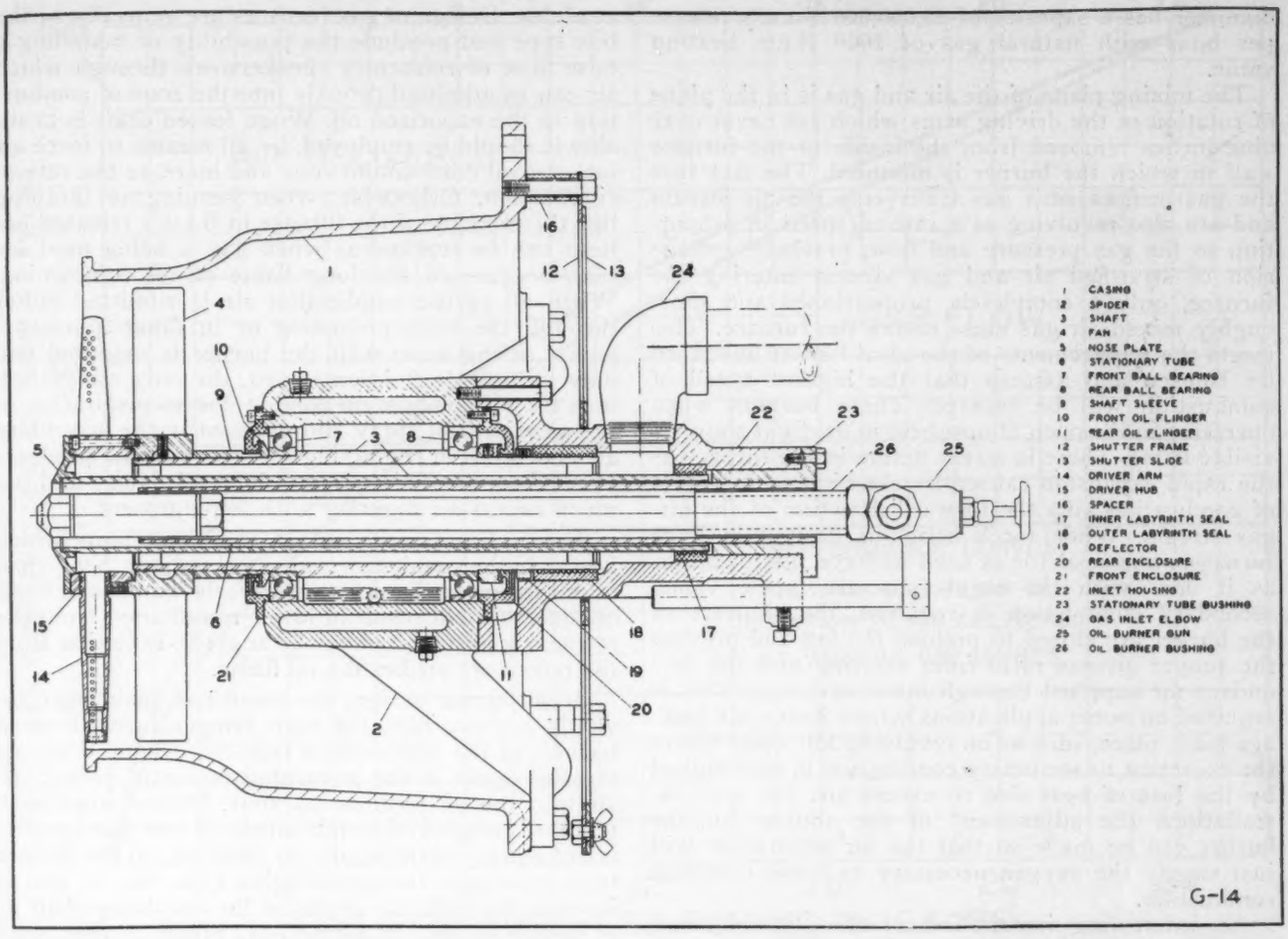
"An ideal gas burner would be one with an infinite number of gas orifices interposed across the air stream."

Analysis of Bunsen's statement means that if the gas orifices of a burner were so numerous and infinitely small that the infinite quantity of gas emitting would immediately enter the furnace with the necessary oxygen in the air stream only primary combustion would occur and therefore the flame produced or region of combustion would be held to the absolute minimum.

Quite a number of burners have been developed in the past few years. A great deal of improvement has been made in the design of air registers to improve the older type ring burners and center fired diffusion type. The advent of improved types of partial premix burners (essentially the Bunsen Type) has shown up advantageously and has been received favorably by the industry. The premix burners where

The drawings show two types of Mechanical Air-Mix Burners





all of the air is premixed with the gas outside the furnace by Venturi injection, proportioning valves, or automatic proportioning and mixing by means of separate power source, are again finding applications in the improved form. Multi-jet designs have recently appeared where the combustion zone can be varied by changing the angle of the various jets. Some of these are of the semi-premixing type while others depend on furnace turbulence together with inspirated air to complete the mixing within the furnace. The maximum working pressure of the gas within the burner manifold for most efficient operation is limited to about 15 pounds gauge pressure.

In 1935 another design was developed that is individual and employs new principles over the conventional designs. It is known as the fanmix type burner, deriving its name from the fact that it is neither of the premix nor multiple jet type, but rather mixes the gas with the air essentially in the plane of rotation of a fan which is propelled by the gas streams emitting from orifices in revolving arms mounted integral with the fan blades. This burner utilizes the energy in the gas due to pressure, to induce air flow into the casing and to overcome pressure drop across the burner. The maximum operating pressure is relatively unlimited. The manufacturers rate the capacities at 25 pounds operating pressure, but over 40 pounds has been used. The effect of pressure on this type burner is only to limit the capacity. On natural gas of 7 pounds pressure the capacity of the burner is about 55 percent of its capacity with 25 pounds pressure. No air can enter the furnace with this burner, that has not been mixed with the gas escaping from the gas orifices. This burner performs mechanical work and operates essentially as follows.

The fuel gas under pressure is conducted to the burner which is mounted in the furnace wall. The design of this burner is built around the characteristics of the fan blades which deliver a known amount of air per revolution to the furnace. The horsepower required to drive the fan from zero R.P.M. to maximum operating speed was determined in wind tunnel tests. Bolted securely to the fan hub which is hollow, spokes corresponding to the number of fan blades are mounted on this hub. These spokes are then drilled with orifices which admit the gas transverse to the air stream. By calculation of the horsepower developed by the gas escaping from these orifices to develop a curve that is parallel to the curve of the horsepower required to drive the fan at the proper speed to deliver air for combustion in the correct amounts, this burner will maintain a constant air-gas ratio against the same furnace draft conditions when operating anywhere from a few ounces of pressure to pressures in excess of 25 pounds per square inch. The curvature of the fan blades is such that the amount of gas at any point from the hub to the extremity of the fan in the cross section is essentially in the same proportion to the amount of air delivered by the fan at that point as at any other point in the plane of rotation of the fan. The driving action of the escaping gas acts as a reaction turbine and the angle of drilling, distance away from the center, and areas of the orifices are the determining factors for the horsepower developed.

A burner of the fanmix type only 21 inches in

diameter has a capacity of 55,000,000 B.t.u.'s release per hour with natural gas of 1000 B.t.u. heating value.

The mixing plane of the air and gas is in the plane of rotation of the driving arms which are never over nine inches removed from the inside of the furnace wall in which the burner is mounted. The fact that the gas orifices emit gas transverse the air stream and are also revolving at a rate of speed in proportion to the gas pressure and flow, precludes admission of stratified air and gas stream entering the furnace, only a completely proportioned and thoroughly mixed air-gas mass enters the furnace. This meets the requirements of the ideal burner described by Bunsen and assures that the highest speed of combustion will be secured. These burners when operating in the open atmosphere in daylight show no visible flame. There is no fan action in the furnace as the rapid expansion caused by the high temperature of combustion kills the forward direction of the air-gas stream. When torch action is desired in huge furnaces, a special tile is used to force this to occur, as it does with the regular premix types. When secondary combustion is required, the shutters of the burner are closed to preload the fan and prevent the proper air-gas ratio from existing and the secondary air supplied through other openings. This is required on some applications where heavy air leakage takes place, such as on revolving kilns and where the objection to secondary combustion is outweighed by the loss of heat due to excess air. On such installations the adjustment of the shutter on the burner can be made so that the air infiltration will just supply the oxygen necessary to cause complete combustion.

An interesting installation of this type burner, which in comparison with the reverse condition cited in the preceding paragraph, is on a rotary kiln that is calcining a product that liberates a quantity of carbon monoxide during the calcining or burning process. To utilize the heating value of the CO produced by the process within the kiln, the fanmix burner has to supply 83 percent excess air over that required for complete combustion of the gas emitting from the burners.

Therefore, it is necessary to know not only the B.t.u. value of the gas, but also the service required and the gas pressure available. With these data the air-gas ratio is established together with the capacity of the burner. With this information the burner drilling can be established to meet the requirements by definite engineering formulae.

Performance on various applications of these burners show that complete combustion is secured without any danger of incomplete combustion with less than 5 percent excess air present in the flue gases leaving the furnace. Furnace temperatures are higher on the walls and floors than other burners where forced draft equipment is not provided. In a number of installations the heat input has been increased as high as 40 percent without increased temperature of the flue gases. This is attributed to the reduction in excess air together with the increased radiation from the combustion gases and the higher temperatures of the radiant refractory surfaces, resulting in increased heat transfer to the radiant tube surfaces.

COMBINATION GAS AND OIL BURNERS:

It is difficult to economically burn oil in a furnace designed for burning gas with only natural draft available. Design of gas furnaces are generally of the box type and preclude the possibility of installing a false floor of refractory checkerwork through which air can be admitted directly into the zone of combustion of the vaporized oil. When forced draft is available it should be employed, by all means, to force air into the oil combustion zone and increase the rate of combustion. Otherwise, when burning oil nothing like the capacity of the furnace in B.t.u.'s released per hour can be reached as when gas is being used for fuel, because of the long flame of oil combustion. When all of the combustion air is admitted either through the burner opening or in other admission points in the same wall the burner is mounted and only natural draft is employed, the only air getting into the oil combustion zone is due to inspiration of the atomized oil spray and necessarily the secondary air is delayed in contacting the intermediate products of combustion. This tends to long oil flames and too much excess air together with impingement.

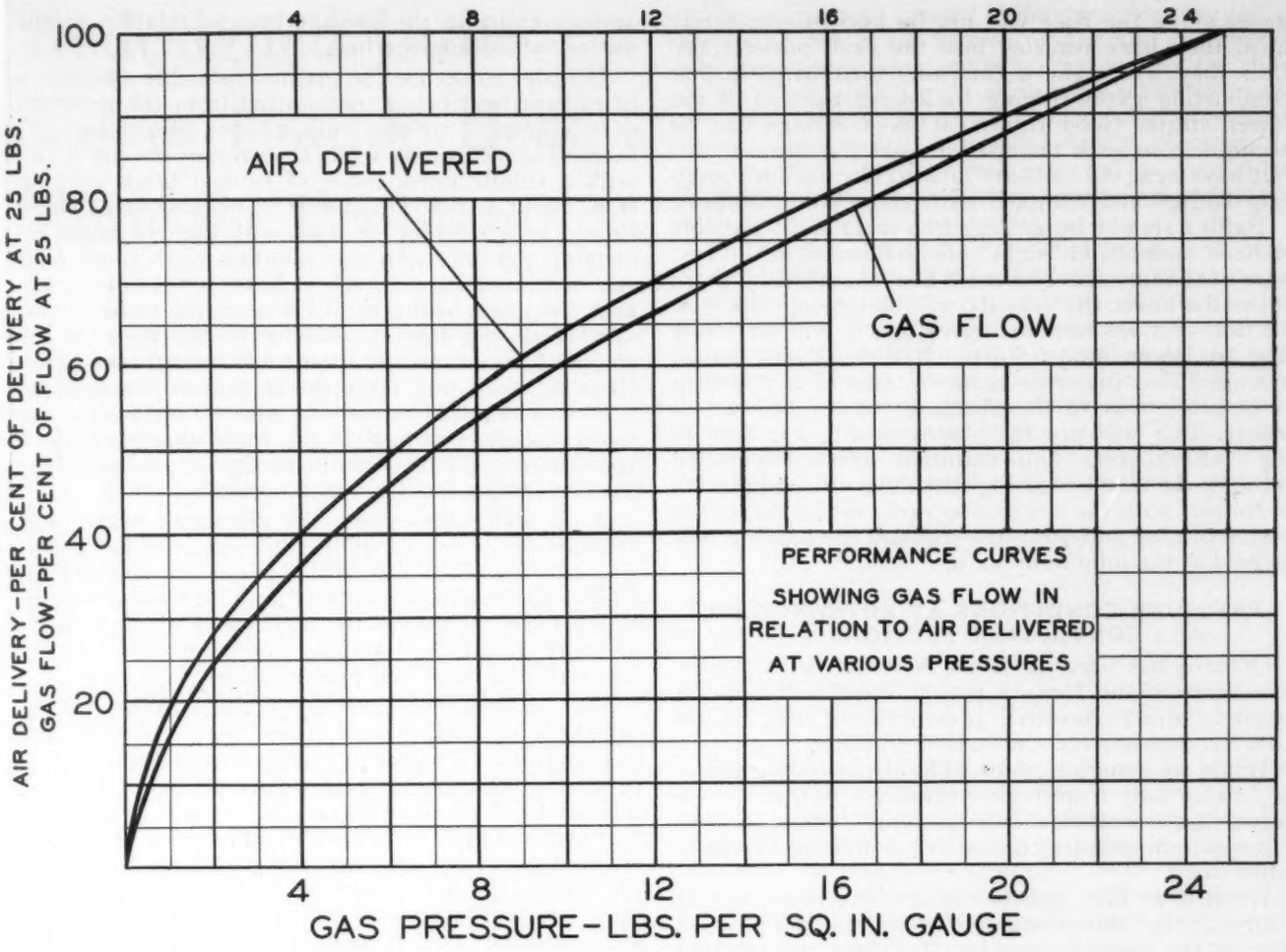
Although oil burns with a luminous flame which has a higher emission value of radiant heat than does the non-luminous gas flame, the flame is in itself opaque and will result in lower re-radiation from the refractory surfaces when the angle of radiation from the refractory strikes the oil flame.

In oil burner design, the trend has again been towards a short flame of high temperature. In most burners of the combination type the design of the air register again is the governing factor to propel the air into the oil combustion zone. Unless some such feature is employed, combination oil and gas burning is not equally satisfactory on furnaces. In the fanmix type burner, of the combination type, the oil gun is inserted through the center of the revolving shaft as is shown on the drawing G-14. Steam is then used to propel the fan instead of gas and this furnishes forced draft and brings about quick combustion of the vaporized oil, resulting in a very short oil flame. This allows a furnace to have as high a capacity on oil in B.t.u. input per hour as on gas, without flame impingement. It is not necessary with this type burner to cause all of the air to go through the burner in forced draft and some may be admitted through openings below the burner in the wall in which the burner is mounted. This reduces the amount of steam required to drive the fan. Other satisfactory installations have been made by mounting the oil burners over the regular fanmix burner in separate openings so the atomized spray of oil is injected into the furnace at a downward angle to intersect the air stream of the fanmix burner, created by propelling the burner with steam, at a point about four to five feet in front of the wall of the furnace.

For most economical operation of any combination gas and oil burner, forced draft by electric motor-driven fans or steam turbine-driven fans, when the latent heat of the exhaust steam is recovered, should be given a survey and engineering economics used to determine if these means should be employed.

AN UNUSUAL APPLICATION:

Recently, at the suggestion of Dr. C. W. Rippie, of Solvay Sales Corporation, an interesting test application was tried with the combination type fanmix burner. One of these burners was installed in the open and connected to a gas supply line. The regular oil burner was then inserted and the oil valve connected to a pump that was drawing spent caustic solution from a tank. The burner, being of the steam



atomizing type, was then connected so gas would serve as the atomizing medium for the spent caustic solution.

Gas was turned on the burner and ignited. This produced a region of high heat intensity but no visible flame. The oil gun then was used to inject gas atomized caustic solution into the inner area of the combustion zone.

Flash evaporation occurred at a rate of evaporation of approximately 200 gallons per hour and the burned caustic deposited on a metal sheet placed in front of the installation as a white powder.

While this installation was rather crude, it indicated that this might well be a feasible way of eliminating the nuisance now present due to collection of spent caustic solutions which cannot be dumped into streams. It is possible that recovered spent caustics from this source might be of value in the paper industry and offset the fuel cost required to carry out the process.

Plans are being formulated at this time to get a plant into operation on this service on a commercial scale.

FURNACE AND BURNER RELATIONSHIP:

Some of the designers of furnace equipment are now designing their furnaces to meet the performance of the burners they supply. Also, some of the gas burner manufacturers are paying more attention to the engineering of burners to meet the conditions of the furnaces. These two, coordinating together, can render the industry an invaluable service.

No furnace or burner installation should ever be made as a matter of fact. The burner characteristics and furnace characteristics are worthy of engineering study if conservation of fuel and highest efficiencies are desired, together with maximum capacities and freedom from undue maintenance are expected.

In this presentation we have, as simply as possible, tried to bring out the characteristics of combustion and the mechanisms of heat transmission to establish how important the above statements are. No burner should be condemned if it is improperly engineered to the job, nor should a furnace be condemned if improperly supplied with products of combustion.

BAFFLES

The purpose of baffles is to govern the path of the products of combustion of the burners through the furnace and then through the heat absorbing elements. Improper baffling can destroy balanced heat absorption by the radiant tube areas, cause short circuiting of gases before combustion is complete and otherwise not only cripple the burner performance but greatly reduce the efficiency of the unit.

In general, baffles should be designed to avoid "dead pockets" in the furnace. When gas burners deliver a poor mixture of air and gas under jet velocity towards the rear of the furnace and along the floor of the furnace, due to partially unburned gases being relatively cool in comparison with the products of combustion, dead pockets are not so objectionable. This, because the slow burning heavy

gases along the floor will not be burned completely until they have traveled into the dead pockets and thus they will make a "hairpin" turn with the hot combustion gases coming back over the top of the lower strata. Good results at fixed ratings can be secured from such installations but the furnace will not have near the capacity of a similar furnace properly baffled and equippel with short flame burners.

Baffles should be arranged to include all possible radiant surfaces, in "sight" of the furnace, in the first pass of the furnace. The more heat absorbed by these tubes the lower the velocity will be through the convection sections and the stack losses will be lower due to lower temperatures. Baffles should be so arranged that the cross sectional area of any section is in proportion to the absolute temperature at all points. This will prevent obstruction to gas flow in the baffled areas and maintain uniform velocity through the tubes, assuring that the gases will remain in contact with the convection surfaces the maximum period of time and draft loss through the baffling will be held at the minimum point.

PRESSURE CONDITIONS AT ENTRANCE TO CONVECTION SECTIONS

Often it has been observed that even with a positive draft in the furnace proper there will occur a negative draft (positive pressure) in that region directly entering the convection sections.

While we generally think of fluids, including gases, as flowing only from higher pressures to lower pressures, just as heat flow is from a high temperature to a lower temperature, the above condition is easily understood.

When a *positive* pressure exists beyond a point in a furnace that shows negative pressure and a positive flow of the gases known to take place towards the pressure zone, it indicates that the gases are cooler and heavier in the furnace than at the point of pressure and therefore, will displace the hotter gases by convection. This condition in a furnace indicates that combustion is so delayed by the burners that the combustion gases have not been reducing in volume and density due to heat absorption by the radiant surfaces as should be the case. The products of combustion from a burner should, when properly engineered with the furnace, continually decrease in *volume* and *temperature* for maximum heat transmission.

FURNACE FLOORS AND WALLS

In discussion of radiant heat it was established that the quantity of heat radiated by a surface was predicted on the intensity of radiation, the areas involved, and the cosine of the angle relative to the surface emitting the radiant heat in relation to the surface absorbing the heat.

In order to secure the greatest possible advantage of radiant heat being transmitted from the products of combustion to the radiant heat absorbing surfaces, it is well worth while to cover all smooth floors with a rubble finish made of broken brick ranging from about ¼ brick to almost ½ brick in size. These should be placed on the floor with pointed edges up forming pyramids. In this manner much more heat can be transmitted to the radiant tubes. The same area and angle will prevail for directing radiant heat *upward* to the tubes directly over the floor as the projected area *normal* to these tubes remain unchanged. However, with wall tubes the amount of transmission is *greatly* increased as the side areas or surfaces of the rubble are more normal to the walls, that is, angle ϕ approaches zero, and the quantity of radiant heat directed then is increased as ϕ decreases.

If no wall tubes exist, the refractory walls will become hotter due to the greater radiant heat transferred by the sides of the rubble floor and this in turn will be re-radiated in increased amounts proportionate to the fourth power of the increase in absolute temperature angularly into the tube bank to surfaces that can not "see" the radiant floor.

Also, in order to work the entire surfaces of the periphery of radiant wall tubes more uniformly on gas and oil fired furnaces, too much attention cannot be paid to the amount of refractory wall area exposed directly to the radiant heat of the furnace. If furnaces that are now fired with gas and oil have no refractory between the tubes and extending at least flush with the face of the wall tubes on the fire side, improved operation will be secured by installing what is known as "innertube" tile. In boilers with water walls this is paramount if extreme ratings are desired. If consideration is given to the mechanisms of radiant heat transfer, convection and conduction, this will be readily apparent. (See Figures 2 and 3.)

In conclusion, the industry can look forward to continued improvements in heat transfer equipment and burners purchased in the future, but meanwhile, it is well worth the effort to survey old or present equipment with the idea that by minor changes in settings and/or installation of more modern burners, not only can material savings in fuel be affected, but maintenance greatly reduced as well as increased capacities secured. This will often result in a payout for the expense involved in a very short time. Very often revamping existing equipment pays a greater return on money invested than purchase of new equipment.

Redesigned Unit Solves Double Heat Transfer Problem

THE cooling of products in refineries has always been one of the major problems. At the same time, boiler-feed-water heating has been of prime importance, requring considerable outside heat if the temperatiures are elevated at the injection point. Both of these problems may be solved profitably and with little operating expense if the proper type of equipment with adequate capacity is installed.

Rock Island Refining Company, at Duncan, Oklahoma, encountered both problems. The first involved the cooling tower and water circulating pumps, which were under capacity to be successful in bringing about a satisfactory reduction in temperatures. The boilers had been operating favorably with cold water feed, heated by exhaust and process steam, but fuel consumption was excessive. The first problem could have been solved by increasing the size of the cooling tower, and installing larger pumps. To obtain a greater source of power, the boilers would require harder firing, and perhaps the addition of another unit.

The problem was solved, however, without additional operating expense. One of the commodities in the refinery was handled at 80 gallons per minute, with a cooling tower temperature of 625° F. which was reduced to operating temperature with water circulated over the tower. At the same time, the boilers required make-up feed of 80 gallons per minute at a temperature of 80° F. The commodity, a 20° A.P.I. refinery product had a viscosity of .43 centipoises at 440° F. and passed through the processes at 35 pounds operating pressure. The water for boiler feed was pumped to the boilers at 300 pounds operating pressure by reciprocating steam pumps in the boiler room.

To accomplish the solution, 9 exchanger units were installed on concrete piers outside the boiler room, connected in 3 parallel banks of 3 each in series. These exchangers are 22 feet, 8¾ inches overall length, having a maximum width of 9¼ inches each, and stand 3 feet, 4½ inches high. The outer shells are 3-inch standard weight seamless steel pipe, and the inner tubes of 1½-inch I.P.S. seamless steel pipe fitted with steel fins to accelerate exchange of heat.

The atmospheric units in the cooling tower, which had been used to reduce the temperature of the 20° commodity, were left in place, and piping extended from this point to the exchangers. A header was flanged to the upper three connections of the exchanger banks to allow the product to pass downward and emerge from the lower side, flowing through the 3-inch exterior piping, and return to the atmospheric units in the cooling tower for finishing the reduction of temperature. The piping was run overhead, carried on steel posts and supported by brackets welded to the side of the posts. Adequate by-passes were included in the arrangement to control the commodity flow through the exchangers and the finishing coolers.

The water was carried through piping flanged to the lower side of the interior piping and emerged at the top connections, counter current to the flow of the commodity. Connections were provided to use the cold make-up water for condensation of exhaust steam, if necessary, before passing it through the exchangers. A by-pass was provided at the boiler-feed water header to permit continuous operation, with or without the exchangers.

The results obtained by these exchangers were reflected in an increased efficiency of the cooling tower; a reduction in the fuel requirements for the boilers, and a general improvement in the operation of the plant as a whole, including a sharp rise in the temperature of the feed water entering the boilers. The amount of heat exchanged from the 20° A.P.I. commodity to the boiler-feed water by the 925-square foot exchanger installation amounted to approximately 8,000,000 B.t.u.'s per hour on the following operating basis:

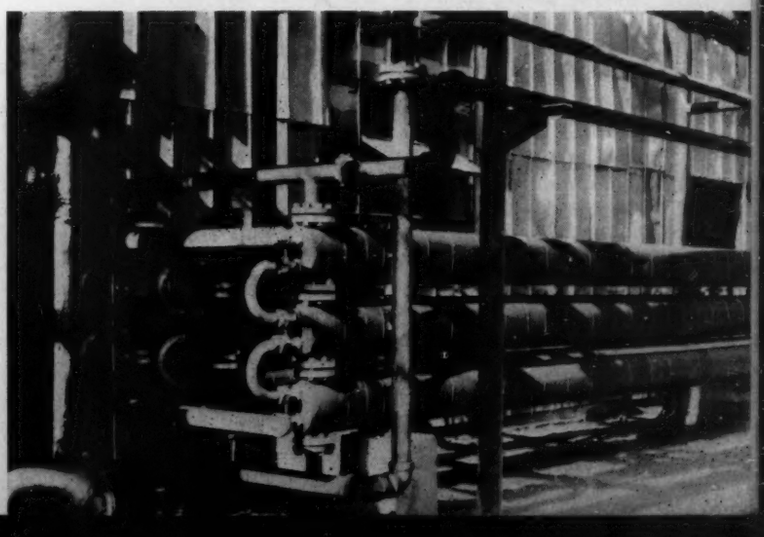
OPERATING DATA

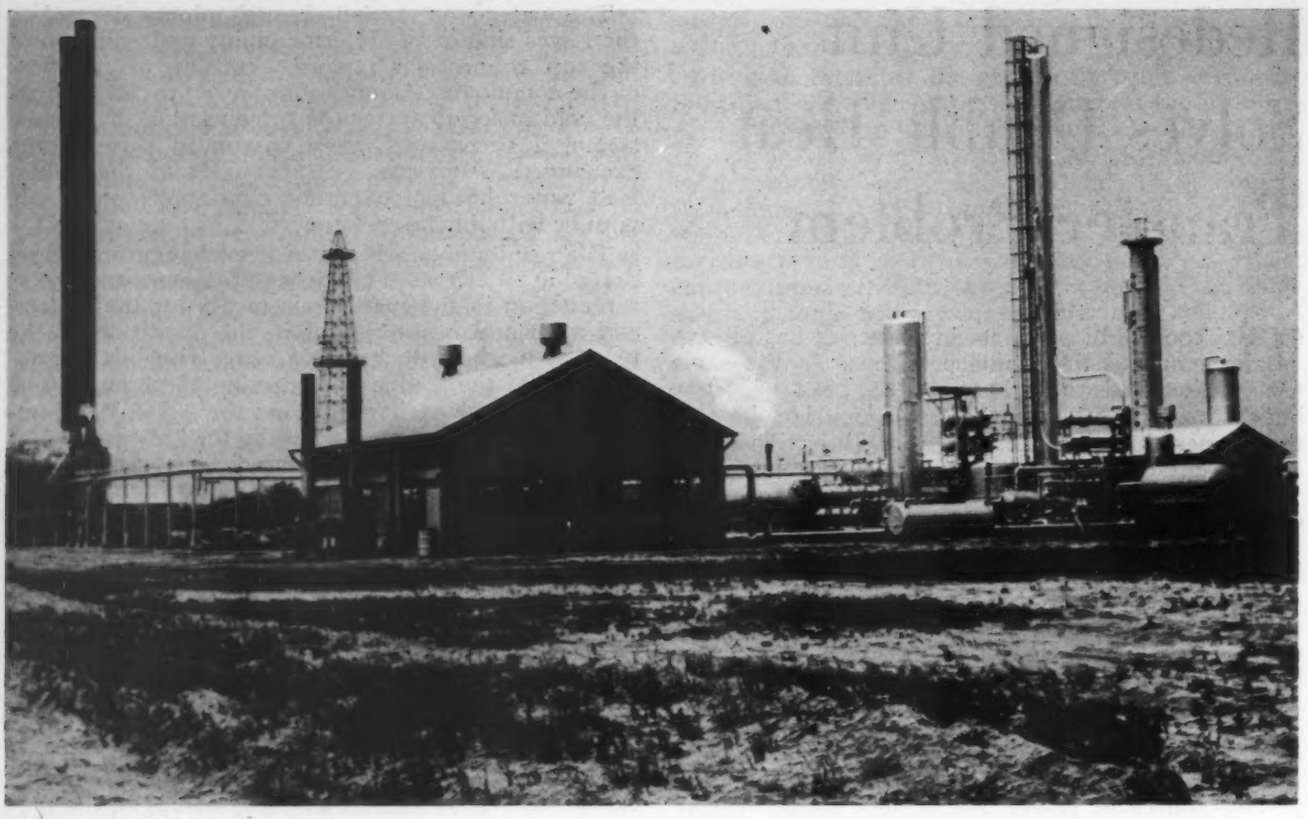
Commodity	Boiler Feed Water
20° A.P.I. product.	Zeolite treated.
80 gallons per minute.	80 gallons per minute.
35 lbs. operating pressure.	300 lbs. operating pressure.
625° F. inlet temperature.	80° F. inlet temperature.
275° F. outlet temperature.	315° F. outlet temperature.

The commodity, after being reduced in temperature from 625° to 275°, was easily cooled in the previously operated atmospheric sections to the temperature required for efficient refinery operation. There is no reason to operate a boiler-feed water heater to raise the temprature of the water prior to its entry into the boilers, as the 8,000,000 hourly B.t.u. transfer is directly into the water, and is not lost through radiation from unprotected piping.

The expense of operating this unit of exchangers is practically nil, and with a clean commodity, and scale-free water, there is no reason that service will be interrupted by periodic cleaning. As the fuel burned in the boilers is a heavy residuum, no measurement is taken of the amount required before or after the installation, but it is stated that the controls on the burners were pinched immediately after the exchangers were placed on stream, and that the fires were appreciably lowered.

The cost of the exchanger unit, computed on a basis of commodity throughput should not exceed 75 cents per barrel. Assuming continuous operation for a year, the amount of commodity passed through the unit for that period would amount to about 985,000 barrels, which would make a yearly barrel cost of about 2¼ mills.





Before Winter Comes

INGENUITY has its ways of whipping old Jack Frost in refineries and natural gasoline plants. Give plant personnel some discarded oil drums or pieces of pipe and a welding machine and equipment, which will freeze unless protected, takes its place as trouble free working parts of the process.

Steam traps, steam pumps, liquid expansion valves, orifice meters, bleeder valves, residue vacuum lines, drain connections and control valves are the equipment most often taken out of commission by subfreezing temperature.

The trend in protective equipment is toward permanent installations. Men with the ingenuity to devise something to hold desired temperature also want something that need not be reconstructed each year.

The time to make the installations is before winter comes.

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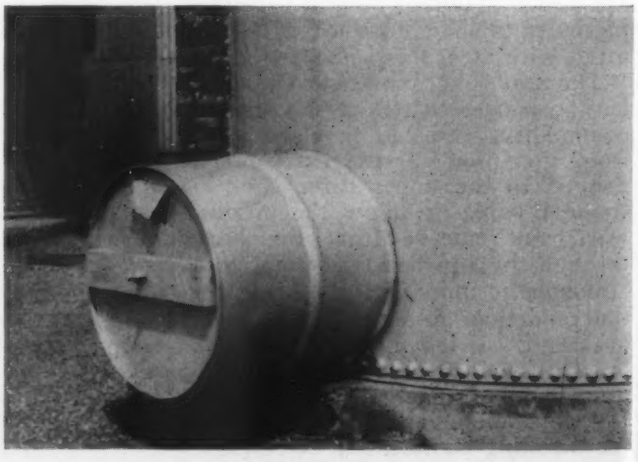
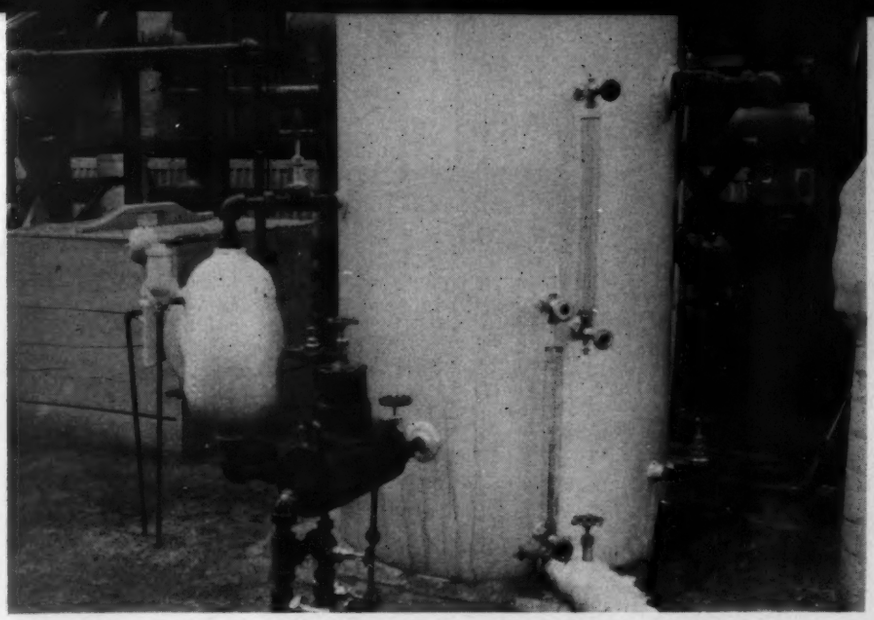


It's the discarded oil drum plus cotton seed hulls that keep freezing temperature away from the water drain line and valve at the base of the gas scrubber at the Earlsboro, Oklahoma, natural gasoline plant of the Barnsdall Oil Company. The open end of the drum is fitted against the base of the scrubber and held in place with a bolt from the valve body to a block outside the closed end of the drum. This end has a door large enough to permit operation of the valve. The installation is complete with a supply of cotton seed hulls and paint to match the scrubber coat.

Before Winter Comes



Above—Enclosures of line pipe surround the drain valves and piping of accumulator tanks and other vessels at the Hollis, Oklahoma, plant of the Lone Star Gas Company. Gates and piping, made up in assembled units, are covered with 4-inch or larger pipe, closed at each end with flat heads, through which process piping is welded. Valve body and packing gland are housed in a dome with a flat head, through which the neck of the valve is brazed. Steam line and water drain lines are provided at top and bottom of each assembly. By holding sufficient back pressure on the jacket, heat may be introduced. The installation is permanent and waterproof.

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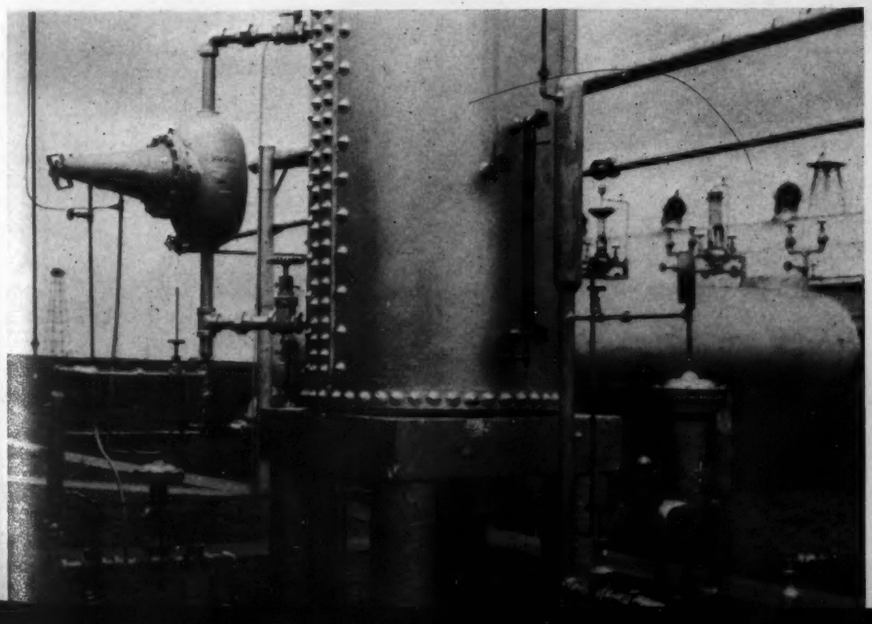
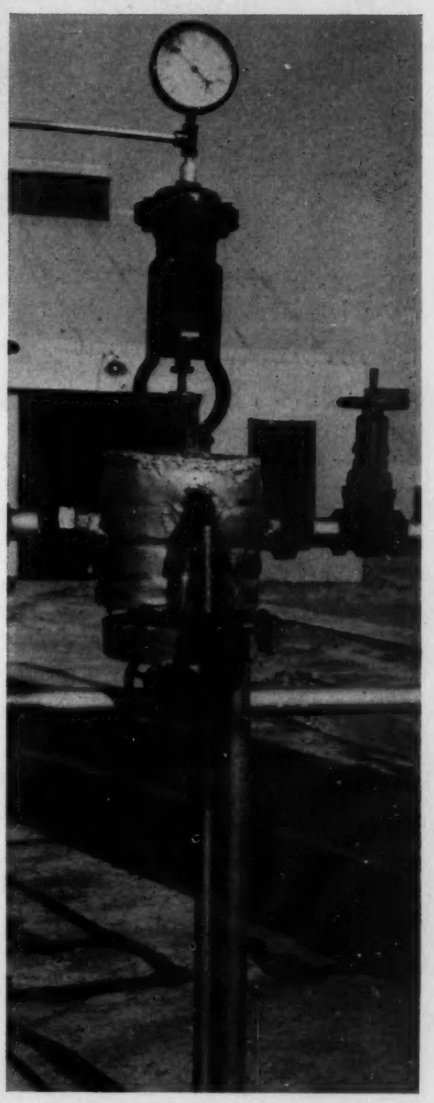
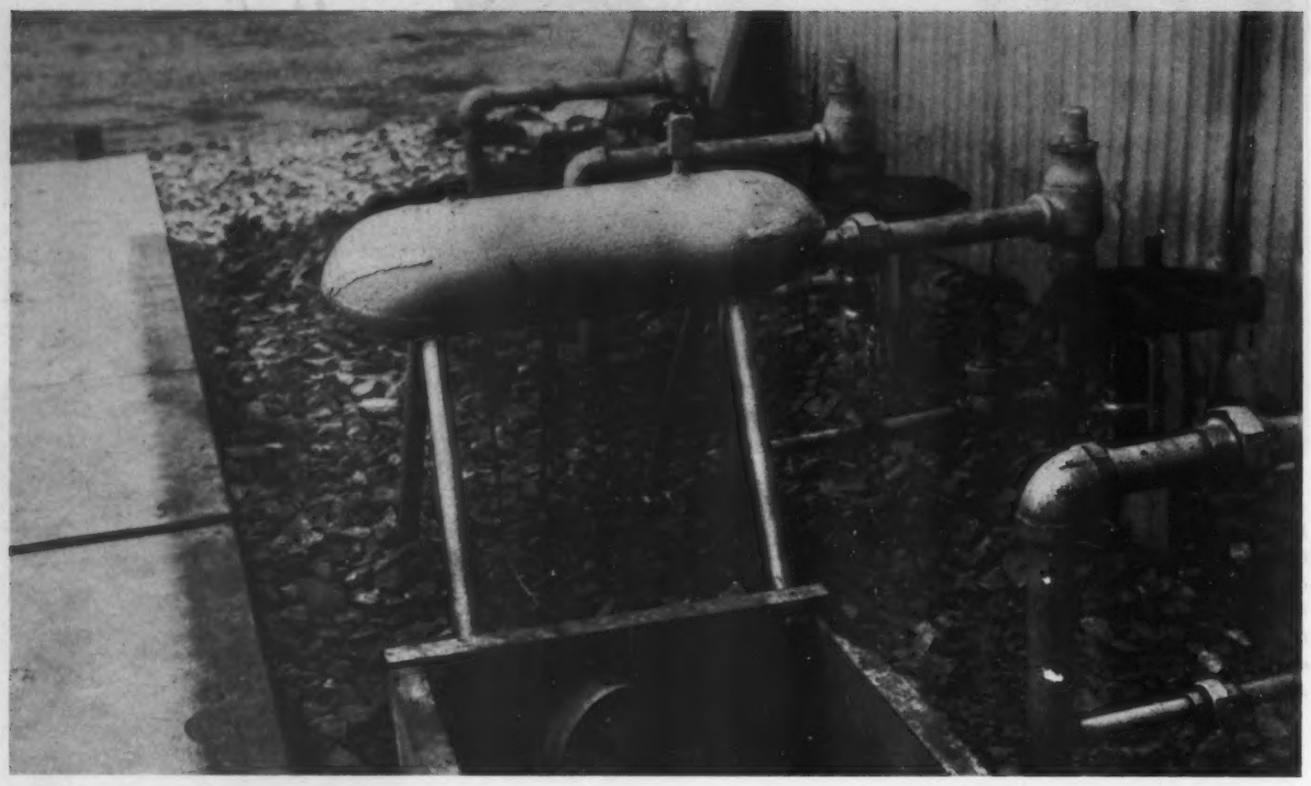
Below—Jacket heaters have replaced wrapped insulation on expansion and outlet valves on high pressure accumulators at the Watkins gasoline plant of Skelly Oil Company, Borger, Texas. Each jacket has a steam coil for maintaining above freezing temperature. Uncondensable gases from the top of the accumulator pass through a 2-inch line in which the control valve is located. For the liquid outlet only a 1-inch line is required. This has a float control. Protection for the gas line control is a nipple of 3-inch pipe, to jacket the vapor line just above the outlet of the pressure control valve. A jacket of 2-inch pipe is welded in similar position around the liquid line. The two jackets are connected by quarter-inch pipe. From the plant header steam is introduced in the larger jacket and flows next to the smaller jacket. Condensate and unused steam enter the exhaust system leading to the boiler feed tank. Adjustment of one valve provides heat for continuous temperature control.





Above—A coil of small piping around the propane expansion valve, plus sufficient insulation, is the common practice to counteract freezing. Also common to such installations is the mud that comes from dripping condensation or steam. Insulation method for these valves is no departure in the gasoline plant of the Deep Oil Development Company in the K-M-A field. There is a departure, however, in the drip pan and drain line for each valve. The pan has sufficient space between the valve to allow cleaning and provide circulation.



Above—A "shot of alcohol" (industrial) keeps residue and vacuum lines open around the Naval Reserve gasoline plant of Skelly Oil Company. The equipment is a blow case, also known as a "boll weevil." The device was made by welding the ends of a short piece of pipe to form a pressure vessel. Legs were welded to give proper height. Two nipples were provided underneath and one above, this one for filling the container. Needle valves were provided on the lower nipples and copper tubing from the valves into the line being serviced. One nipple on the lower side was long enough to have its upper end above the liquid level inside the container so pressure could be equalized and the amount of alcohol metered as required.

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Before Winter Comes

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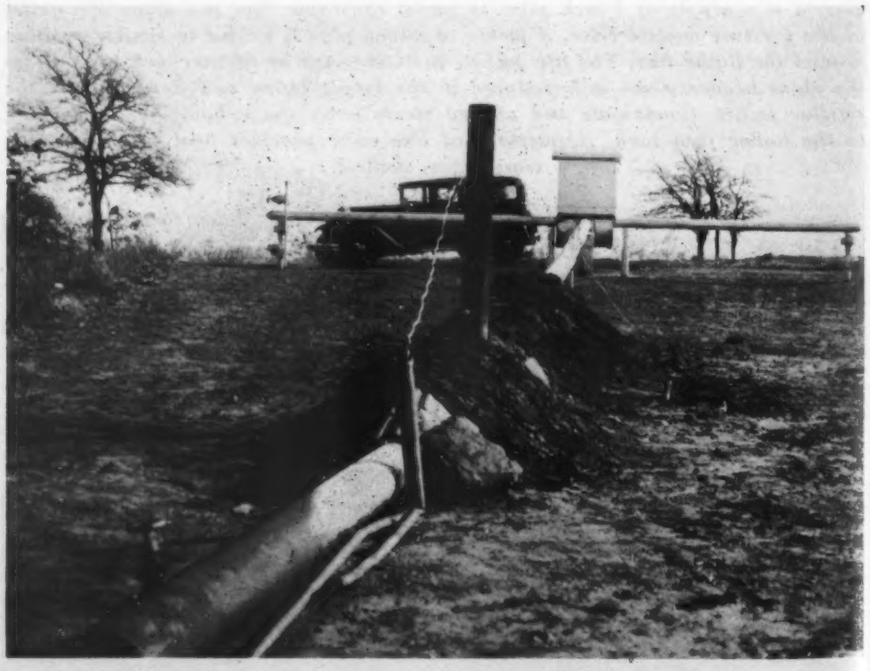
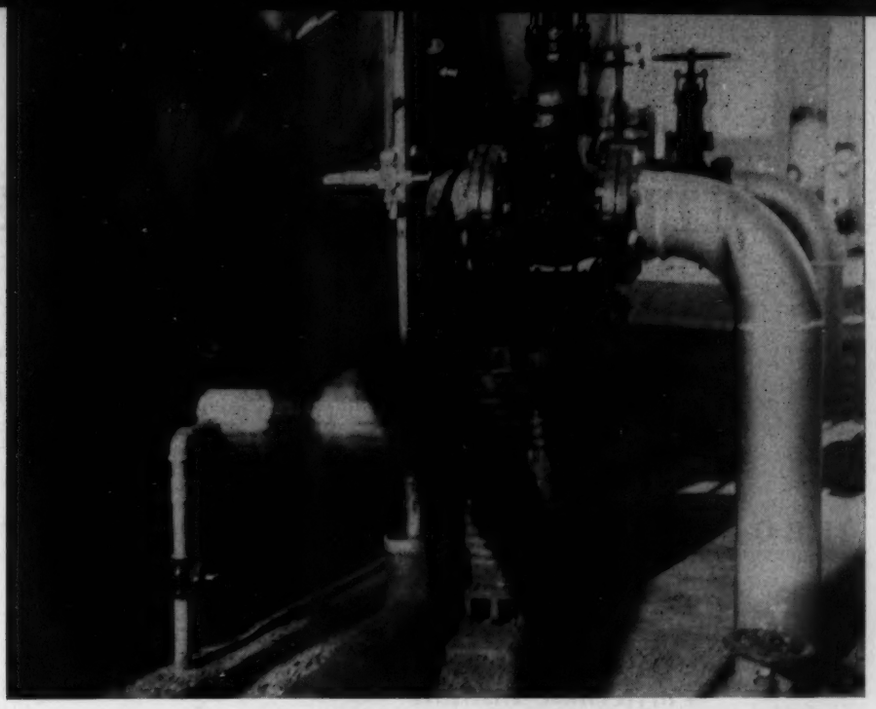
Below—When there is ice around the orifice the meter recorder tells a sorry story. There is none of that on meter settings of the Coline Gasoline Corporation. The device takes advantage of prevailing winds to pour heat around the orifice flange. First the flange was covered with a discarded oil drum. This was connected to a section of pipe, which was insulated. At this point a typical oil field heater was constructed by running this pipe through a larger one and a stack provided. The large pipe was extended a short distance, so air could be used for carrying the heat to the meter run. Prevailing winter wind in the instance illustrated called for the end of the open pipe to extend in that direction.



Before Winter Comes



Above—Cylindrical jackets around the water drains for absorption oil and live steam nozzles into the jackets are the answer to frozen and ruptured connections in the Rodessa natural gasoline plant of the Coltexo Gasoline Corporation. The steam piping is connected to the live steam header. Each jacket is manually controlled.

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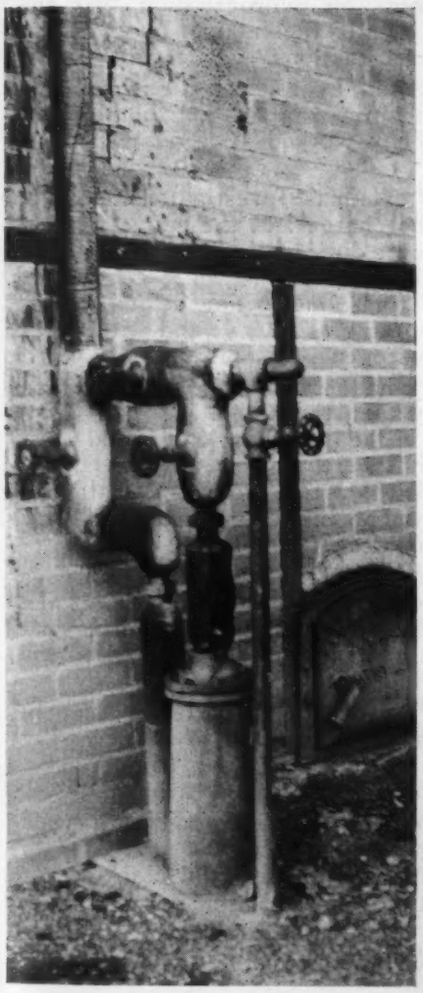
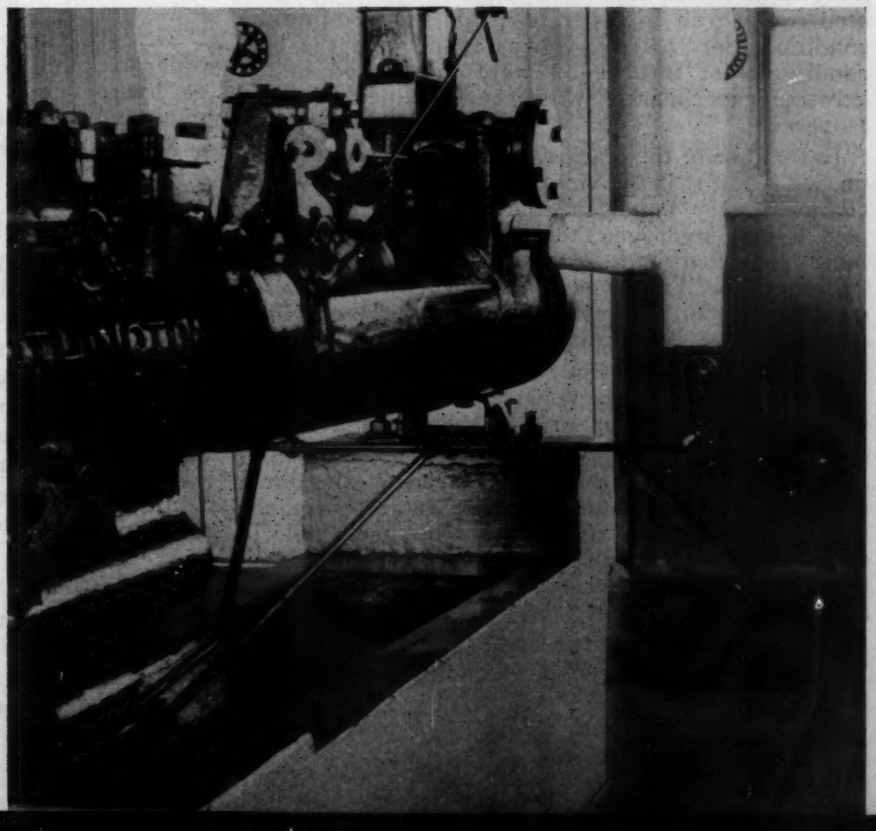


Above—Outdoor steam trap installations of the Talco Asphalt and Refining Company plant, Mt. Pleasant, Texas, are housed in metal jackets. A section of pipe, large enough to surround the trap and small enough to prevent the flanged end from passing through the jacket. A flat steel plate is set below both, usually on the ground to prevent air circulation. The whole assembly is insulated with magnesia or asbestos.

Below—For protecting the idle steam pump, Skelly Oil Company, Fairfax, Oklahoma, has a drain manifold, connected to the pet cocks on the steam cylinders as well as to both the live steam line below the throttle and the exhaust line near the pump. Both steam lines, live and exhaust, are carried overhead to make risers to and from the pump. Where the lines turn to connect to the body of the steam end, tees are installed with the lower ends fitted with either swedge nipples or reducers. Quarter inch black pipe with valves, closed while the pump is operating, become a drain when the valves are opened with the pump idle. The assembly may be made as a manifold so water can drain through one line into a sewer.



Destructive Hydrogenation of Residuum Oils *from Roumania*

PROF. DR. ING. C. CANDEA
and
DR. L. SAUCIUC

Of the Chemical Laboratory of Timisoara Polytechnic Institute

CONTINUING our research on hydrogenation of various Roumanian petroleum oils,[1] we will describe the hydrogenation of oil residuum from Bucsani (Roumanian crude oil). These crudes are especially interesting since their chemical composition appears to be different from the average. Previously we had shown that the course of the hydrogenation reaction is closely connected with the chemical composition, while simple hydrocarbon groups behave differently in the cracking-hydrogenation reaction.

The behavior of simple oil fractions in destructive hydrogenation was followed in the same apparatus, under similar conditions, and we treated kerosines, furnace oil and paraffin in this manner in order to draw some conclusions concerning the reactions that take place.

After we had shown that kerosine can be converted into 50 percent of low-boiling hydrocarbons at 300 atmospheres pressure and 430° C. temperature with molybdenum sulphide catalyst, we then hydrogenated furnace oil in order to establish the optimum conditions for this oil. It was found that the best conditions for furnace oil were those used in the kerosine experiments, while the gasoline yield was 44 percent.

In the case of the cracking-hydrogenation of paraffin, we found that the volume of the space above the charge is very important, since this space is occupied by the hydrogen, the reaction products being more saturated with greater excess of the initial hydrogen gas employed; molybdenum sulphide is also a very good catalyst with paraffin; the gasolines obtained at 430° C. using 200 atmospheres pressure were saturated products.

Before describing our experiments with residuums, we will first report on some of the newer literature references on this subject.

C. C. Hall and Crawley,[2] comparing aluminum oxide and molybdenum sulphide catalysts in the hydrogenation of low temperature tar, were able to show that molybdenum sulphide will secure a much higher content of saturated hydrocarbons than will aluminum oxide.

J. Kosaka, Yananouchi and Tanaka[3] obtained a gasoline showing 50 percent paraffin, 25 to 30 percent naphthenes and 15 to 20 percent aromatics working at 470° C., and hydrogen pressures of 90-100 atmospheres in the presence of Ni_2O_3, WO_3, and $ZnCl_2$.

V. N. Ipatieff[4] draws the conclusion from his results and experiments on hydrogenation that the fineness or particle size of the catalyst plays an important role in these reactions.

N. Kishi and M. Ando[5] hydrogenated Fushuu shale oil with Mo, Cr and iron catalysts and obtained 10 percent gasoline. They worked at a relatively low temperature of 270° C.-350° C.

G. Morgan and J. Thomas[6] investigated the effect of the motion of the charge and the active stirring effect of the hydrogen during the hydrogenation in pipe coil systems. They obtained from coal-tar fractions 18 percent of a gasoline boiling below 200° C. (with gas) when working at 560° C. and with about 200 atmospheres hydrogen pressure.

P. V. Pouchkov[7] had shown that the paraffins split-up more easily than the aromatics, in destructive hydrogenation in the liquid phase at initial pressures of 80-100 atmospheres and at 450° C. Higher pressures are needed for the aromatics. Catalysts likewise are employed in this case which will drive the splitting of aromatics to completion.

The same author[8] subjected various oil fractions to destructive hydrogenation at 100 atmospheres and 450° C. temperature, and found that the chemical composition of the end product was related to the nature of the starting material.

M. S. Nemtsev[9] made the observation that in order to obtain high-octane gasoline, it was necessary to hydrogenate a starting material containing a minimum amount of paraffinic hydrocarbons.

N. Kishi, M. Ando and J. Esaki[1] worked with crude oils, hydrogenating them between 200 and 380° C. At 200° C. they observed a very mild cracking; at 330° C. the density of the reaction product rose, interpreted as the beginning of polymerization reactions, while at 380° C. cracking was very pronounced.

G. Pastonesi[11] subjected a distillate from Albanian crude to hydrogenation at 200 atmospheres and at 425-500° C. temperature with catalysts and showed that naphthenes and aromatics increase with the rise in operating temperatures.

The many patents in this field specify conditions and cover the use of catalysts for various products.

EXPERIMENTAL

The starting material is the residue from Bucsani crude above 330° C. Bucsani crude shows a specific

TABLE 1

Exp. No.	° C.	Hydrogen Pressure			Charge	MoS_3 Cat. Percent	Yield Gms.	Den. 15° C.	Engl. Distillation (Percent)					Analysis of Benzine to 150° C.				
		Init.	Max.	Final					Init.° C.	150° C.	175° C.	200° C.	300° C.	Den. 15° C.	Percent Hydrocarbons			
															Unsat.	Arom.	Naph.	Sat.
1	430	125	300	90	150	..	135	0.834	42	18	22	27	45	0.706	4	9	27	60
2	430	25	135	29	150	10	130	0.832	35	26	35	42	65	0.703	4	10	27	59
3	430	45	195	40	150	10	130	0.830	37	27	35	41	64	0.704	4	10	31	55
4	430	90	268	62	150	10	130	0.822	42	26	32	37	61	0.701	3	7	27	63
5	430	110	283	78	150	10	130	0.829	38	26	33	37	60	0.704	3	9	27	61
6	430	125	338	95	150	10	130	0.830	42	25	30	35	55	0.704	3	11	31	55
7	430	100	265	78	100	10	85	0.820	38	30	37	42	66	0.706	3	10	31	56
8	430	117	290	93	100	10	85	0.822	37	30	37	45	66	0.707	2.5	10	30	57.6

gravity at 15° C. of 0.809, contains 7.92 percent wax and an Engler distillation showed:

Degrees C.	Percent
42-75	7
100	11
125	15
150	22
175	28
200	33
225	38
250	43
275	48
300	57
330	60

The paraffin in the crude calculates to nearly 20 percent on the distillation residue.

The experiments were carried out in a non-rotating autoclave of S-M steel of 500 c.c. capacity. The oil was heated until it was quite liquid and well mixed with the catalyst. After placing this charge in the autoclave, hydrogen pressure was applied by a Laud pump, and the apparatus heated to the desired temperature. The duration of the reaction was one hour. One noted the initial pressure, maximum pressure (highest reading during the reaction) and the final pressure obtained after cooling the apparatus.

Table 1 shows the results of these experiments, working at 430° C., and between pressures of 135 to 338 atmospheres using molybdenum trisulphide as catalyst.

Comparing these results, it is seen that when no catalyst is used, the result is an unsaturated product low in benzine; the catalyst operates to produce increased benzine yields. The percent of benzine obtained does not change with the amount of hydrogen employed, and seems to remain constant up to a pressure of 300 atmospheres; at higher pressures, there is a decrease in the amount of distillate.

Saturation is obtained chiefly above 200 atmospheres, while below this pressure the percent of unsaturateds does not seem to vary, whether one uses the catalyst or not.

From the data of the benzine obtained, it is seen that the saturated hydrocarbons decrease with an increase in the initial hydrogen pressure, and reached the lowest value at 200 atmospheres maximum pressure; at higher pressures the saturates again increase with a tendency to decrease at still higher pressures.

As mentioned above, the free space which can be occupied by paraffin seems to enter into the problem. Experiments conducted in large vessels or where the space was unduly large, yielded products indicating deep-seated cracking, and the yields were much better than where the reacting spaces or volume of space above the charge was smaller. These results apply also to the residues. (See Experiments 7 and 8.)

The temperature of 430° C. did not seem to be the optimum for this product, so a new set of experiments (Table 2) were started. Higher temperatures were used and we also varied the quantity of catalyst and the amount of hydrogen.

Experiments 1, 2, 3, 7, without catalyst and also with increasing content of 2.5, 5, and 10 percent catalyst at equal pressures, reveal the effect of percent catalyst on yield of benzine, increasing the yield as the catalyst is increased. The saturateds drop as the catalyst is increased. By a step-wise increase in quantity of hydrogen employed, a further increase in benzine yield could be obtained.

The beneficial cracking action of the catalyst upon our raw charge is further evidenced from the data on maximum pressure, which increases with the increase in the catalyst. A pronounced saturation of the unsaturated cracked products occurs beyond the 225th atmosphere of pressure. Beginning at this pressure and to about 260 atmospheres maximum pressure, there is a decrease in unsaturated hydrocarbons, after which the value remains constant.

Cracking hydrogenation of our residue takes place smoother at 440° C. than at 430° C. (See Table 1). Both temperatures yielded a product of equal unsaturation, but at 440° C., the benzine yield was higher.

One could not operate above 450° C., with the necessary amount of hydrogen, since the pressure upon heating to 450° C. rose above the limits of safety for the apparatus. Despite the low initial pres-

TABLE 2

Exp. No.	° C.	Hydrogen Pressure			Charge	MoS_3 Cat. Percent	Yield Gms.	Den. 15° C.	Engl. Distillation (Percent)					Analysis of Gasoline to 150° C.				
		Init.	Max.	Final					Init.° C.	153° C.	175° C.	200° C.	300° C.	Den. 15° C.	Percent Hydrocarbons			
															Unsat.	Arom.	Naph.	Sat.
1	440	95	280	60	150	..	125	0.831	41	27	33	38	63	0.695	4	8	24	64
2	440	80	280	46	150	2.5	130	0.832	40	28	35	40	63	0.702	4	8	28	60
3	440	80	290	50	150	5	130	0.830	37	30	37	43	66	0.701	4	8	29	59
4	440	25	225	39	150	10	130	0.820	39	28	35	42	66	0.704	5	9	31	55
5	440	50	245	48	150	10	130	0.826	38	28	35	41	66	0.706	4	9	31	56
6	440	65	260	57	150	10	130	0.820	38	31	38	44	69	0.705	3	9	31	57
7	440	80	300	63	150	10	130	0.818	34	32	38	44	70	0.709	3	9	24	63
8	450	40	295	45	150	..	120	0.823	39	36	44	51	73	0.700	4	8	27	67
9	450	25	315	50	150	10	110	0.813	35	39	48	56	77	0.710	4	12	28	56

TABLE 3

Exp. No.	°C.	Hydrogen Pressure			Charge	MoS_3 Cat. Percent	Yield Gms.	Den. 15° C.	Engl. Distillation (Percent)					Analysis of Gasoline to 150° C.				
		Init.	Max.	Final					Init.° C.	150° C.	175° C.	200° C.	300° C.	Den. 15° C.	Percent Hydrocarbons			
															Unsat.	Arom.	Naph.	Sat.
1	430	125	300	90	150	..	135	0.834	42	18	22	27	45	0.706	4	9	27	60
2	430	110	238	72	150	10	125	0.824	45	19	25	30	50	0.712	3	8	24	65
3	430	125	278	85	150	10	125	0.822	40	18	24	28	48	0.710	3	8	24	65
4	440	95	280	60	150	..	125	0.831	41	27	33	38	63	0.697	4	8	24	64
5	440	60	218	45	150	10	125	0.825	41	26	32	38	62	0.709	4	9	24	63
6	440	125	300	78	150	10	125	0.818	38	26	31	37	62	0.707	2.5	7.5	26	64
7	450	40	295	45	150	..	120	0.823	39	36	44	51	73	0.700	4	8	27	61
8	450	80	360	80	150	10	115	0.816	35	35	43	50	73	0.698	2.5	9.5	27	61

sure, this temperature is the optimum condition at which the catalyst exerts its greatest effect on the benzine yield.[8,9] The hydro-product obtained contains (using molybdenum trisulphide) greater amounts of low-boiling fractions than that obtained at 430° C. or 440° C.

In another series of experiments, we investigated the action of molybdenum trioxide as a catalyst.

From Table 3 it can be seen that this catalyst exerts an action different to that of molybdenum trisulphide when one operates between 430 and 450° C.; the action is different both in regards to cracking and hydrogenation.

While molybdenum trisulphide is better for cracking and gives high yields of low boiling constituents, molybdenum trioxide exerts a superior influence on the saturation of the end product even though the yields are lower.

The percentage of benzine in the hydro-product using molybdenum trioxide at 430 to 450° C. is also the same as in the experiments without catalyst, though the saturation is much better when the catalyst is used.

SUMMARY

The results of hydrogenation of residues from Bucsani crude oil indicate that (when operating in a stationary autoclave) only satisfactory saturation of unsaturated end-products formed at 430° C. can be obtained when using catalysts and by the use of a sufficiently high hydrogen pressure.

The hydrogenation takes place much more smoothly at 440° C. temperature, at the same pressures and in the presence of a similar percent of catalyst, obtaining a much higher yield of benzine.

Operating at higher temperatures was not feasible, since the increased cracking reactions caused the pressures to rise above the maximum considered safe for the apparatus.

Molybdenum trisulphide and the trioxide were the catalysts used. The former is a better cracking catalyst and gave higher benzine yields. The trioxide, having a greater hydrogenation action, gave excellent saturated gasolines even though the yields were somewhat lower.

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